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Tomus XXIV

SUPPLEMENTUM

Proceedings of the 10th International Kaolin Symposium
(IGCP Project No 23: Genesis of Kaolin)
held in Budapest, September 3, 1979

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GENESIS OF KAOLIN

10th International Kaolin Symposium
held in Budapest, September 3, 1979

organized by

Central Office of Geology and
Clay Mineral Section of the Hungarian Geological Society

Hungarian Organizing Committee:

G. MORVAI, Chairman
I. VICZIÁN, Secretary
E. MÁTYÁS
F. SZENTESI
GY. VARJÚ
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Acta Mineralogica-Petrographica, XXIV/1980, Supplementum
Proceedings of the 10th Kaolin Symposium in Budapest
3 September, 1979, IGCP Project № 23

PREFACE

The anniversary 10th International Kaolin Symposium organized by the Hungarian Working Group of IGCP Project No. 23: Genesis of Kaolins in Budapest on September 3, 1979, was attended by 59 geologists, mineralogists and technologists from 17 countries. The topics of papers presented at the Symposium varied from description of new laboratory methods on investigation, contributions to mineralogy or geology of individual deposits, classification of kaolins and clays, to discussion of genesis and age of kaolins.

In a way this Symposium rounded up not only the first ten meetings of the Group, but also it was a milestone which marked the end of preparatory stage of the Group's Final Report for the first decade-of the monograph Kaolin.

In the prehistory of the IGCP Kaolin Project is the 1st Kaolin Symposium held jointly with the 23rd IGC in Prague (August 1968). Symposia and excursions in Spain (1972), France and England (1974), Mexico (1975), GDR (1975), Australia (1976), Japan (1976), Spain and Italy (1977) and England (1978) were followed, by six volumes of papers published (one is still in print), together with eight field-guides to kaolin and clay deposits. Summary of results of all Symposia was published in Geological Correlation (M. Bassett, editor, Special Issue for the General Conference of Unesco in Paris, 1978, p. 112—113), in Episodes (1978, No. 4, p. 12—15, Ottawa) and in Věstník ÚÚG (1980, 55, No. 3, p. 174—180, Prague).

Presently the Project has 23 members from 16 countries, and 80 corresponding members from 40 countries of all continents. During the next five years the Group plans to apply the theoretical results of all symposia to the conditions of the developing countries. The criteria for prospecting and methods of exploration of kaolin deposits will be defined. Workshops on kaolin utilisation for young specialistst from SE Asia, Africa and Latin America will be organized. Among other items, kaolin consumption is an indication of the cultural and technological standard in any given country. More kaolin means more porcelain — and better boarding, more paper and bookes — and less illiterate people, more wall — tiles — and better housing, more mineral-wool for insulation — and lower energy losses. Thus the IGCP Project No. 23 will try to help to lessen the main antagonism of the next decades — the growing gap between the industrialized and developing countries.

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Geology of Kaolin Deposits

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KAOLINITE OCCURRENCES IN HUNGARY

E. NEMECZ

In the framework of a concise but brief paper I am endeavouring to summarize and pass into review our knowledge in connection with kaolin occurrences in Hungary, mentioning there where this appears to be necessary the most important steps of the development and the prospection.

Clay mineral prospection started in Hungary on a broader scale at the beginning of the 50's, when instruments essential for their study became more and more widespread. Since the geological bases, to which I shall refer later on in detail, were more favourable to the formation of three-layer clay minerals rather than to kaolinite, prospecting activity in the country was mainly concentrated on montmorillonite, illite and clay minerals of a mixed structure. In addition prospection of kaolin represented a constant source of interest for geologists on account of its industrial importance.

With a view to the fact that the Conference is dealing with genetic questions of kaolin mineral, I myself am limiting my paper to the prospection of this mineral in Hungary and to its results being, however, aware that genetics of kaolinite are inseparable from the investigation and study of the formation of other minerals.

This statement is specially valid for mineral associations of kaolinite occurrences in Hungary, since the majority of industrially important depositions is of hydrothermal origin as against those formations which were brought by surface weathering.

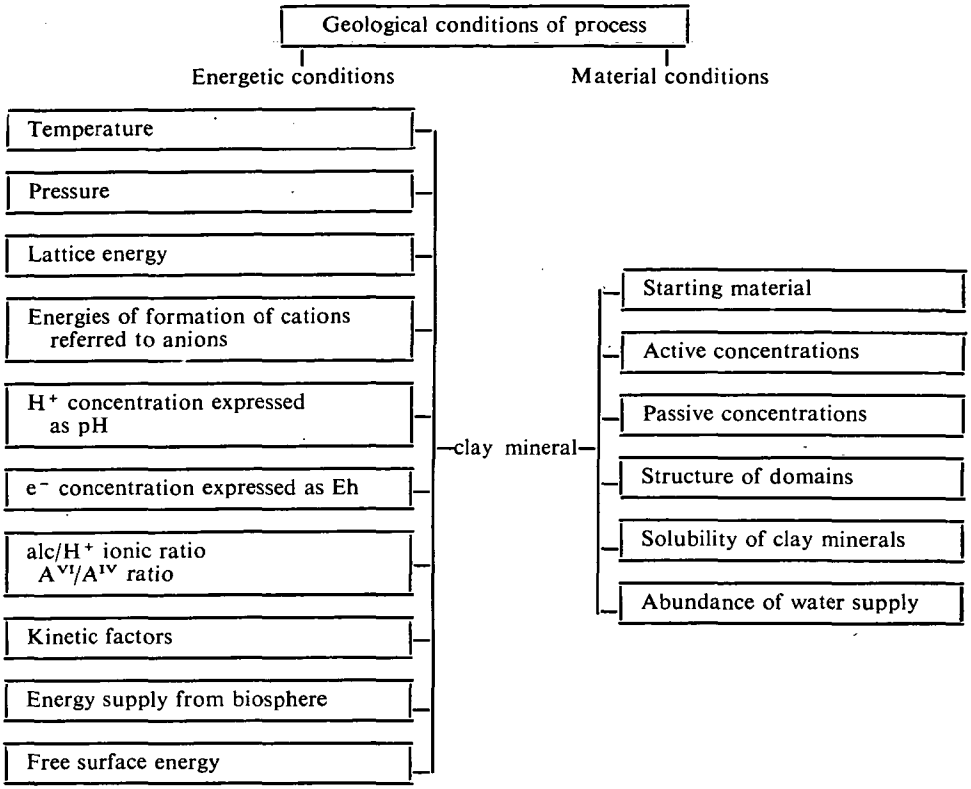
Considering those geological formations in which kaolinite mineral is occurring in whatever a proportion and among some other minerals, we are faced with a rather varied picture. From the point of view of the characteristics of the formation, it appears to cast a light on the material and energy factors of the genetics as well as the geological conditions under which the process took place. All this is shown in Table 1.

Useful information may be obtained to this effect if due consideration is given to the site where the process took place formerly, thus to find out whether it occurred in the 0—5 km zone of the continental crust, on the surface of the continent or in the hydrosphere. In the first case the main process is an epigenetic and hydrothermal alteration, in the second one it is due to weathering, and in the third one it is mainly diagenesis. In the first two cases it is, of course, a primary formation; it is another question again whether the present occurrence of kaolin minerals is as a matter of fact a result of transportation and sedimentation of the primary kaolinite, as well as of process having taken place in the meantime (secondary deposits), which also applies to the third case.

Passing in review the above sequences, hereunder we are explaining kaolinite occurrences and their characteristics in Hungary as follows.

TABLE 1

Physical and chemical factors of clay mineral formation (the author's compilation)



As we have already mentioned, the majority of kaolinite occurrences in Hungary worth consideration are connected with a hydrothermal activity. This circumstance determines the mineral composition of kaolin deposits which is different from kaolinites formed by granite weathering, and the utilization is also markedly different from that.

For the sake of better understanding this peculiarity, let us cast a glimpse on the hydrothermal process itself and let us consider that superheated steam issuing from a zone of great depth, exerts hydrothermal action on a rock. It will dissolve the rock according to its mineral constitution; will saturate with respect to this or that ion, and as a result concentration, Eh and pH parameters determined by temperature and the chemical reactions etc. come to exist. If any crystallization is initiated, its outcome is determined by the actual parameters of the solution. The solution will deposit certain components by crystallization and absorb some others by a dissolving action. Thus, the agency is in a permanent continuous interaction with its material surroundings. The geological process is then very complicated, in this case but as a rule it will not tend to evolve towards any extreme as it has been stated. The overall results is a clay mineral association which belongs to one of several well-defined types, and hence the geological process as a mirror image of

the mineral facies will itself be subject general rules overrinding inicidental conditions.

In conclusion it does not appear to be very remarkable that the number of clay mineral species forming in hydrothermal system — a system that must be regarded as completely open — should be rather small, similar to the number of phases forming from melts, a number determined by the phase rule, since the process in question takes place in a closed system. It therefore appears that even in an open geological system parameters cannot vary quite independently from each other, but on the contrary, their range of variation is confined more and more as the process advances.

Here I would briefly refer to the fact that some authors are doubtful about the possibility of the hydrothermal formation of kaolinite deposits and attribute the formation of deposits to the effect of meteoric water along the fissures. In some of the cases it is indeed a hard job to delimit these two kinds of formations, especially in case if the former seams have come to the surface as a result of erosion. In such cases both ascendent and descendent water effect may be proved on the deposit mixed with one another.

However, those deposits I am talking about at present have doubtlessly been formed in consequence of a hydrothermal effect since they are placed in such a zone-like system which can only be explained with the lawfulness of hydrothermal alterations.

All authors agree that hydrothermal argillization, starting out from the lode, exhibits a zonal geometry dimensions of which are related to the dimensions of the lode. This zonality consists in the qualitative and quantitative distribution of original minerals and alteration products in the individual zones of argillization, implying a flow directed from the lode into the country rock. The flowing medium is water or steam under pressure, probably no hoter than 400—450 °C, which in its course decomposes the minerals formed from a dry igneous melt in succession, according to their relative instabilities. The decomposition products are then reconstituted into phases corresponding to the concentration conditions of the prevailing hydrothermal physical and chemical conditions. The fundamental cause of the zonality being the change in the K/H ionic ratio in the course of the spatial evolution of the process.

Fig. 1 shows the stability area of K-mica to lie between those of K-feldspar and

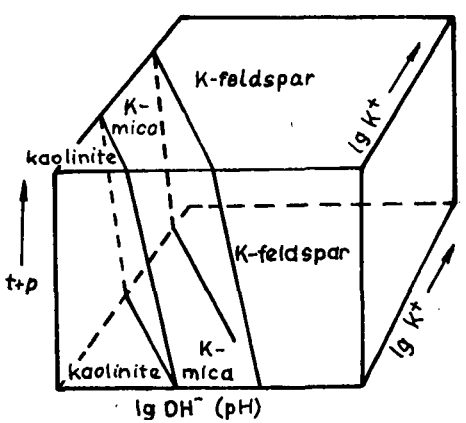
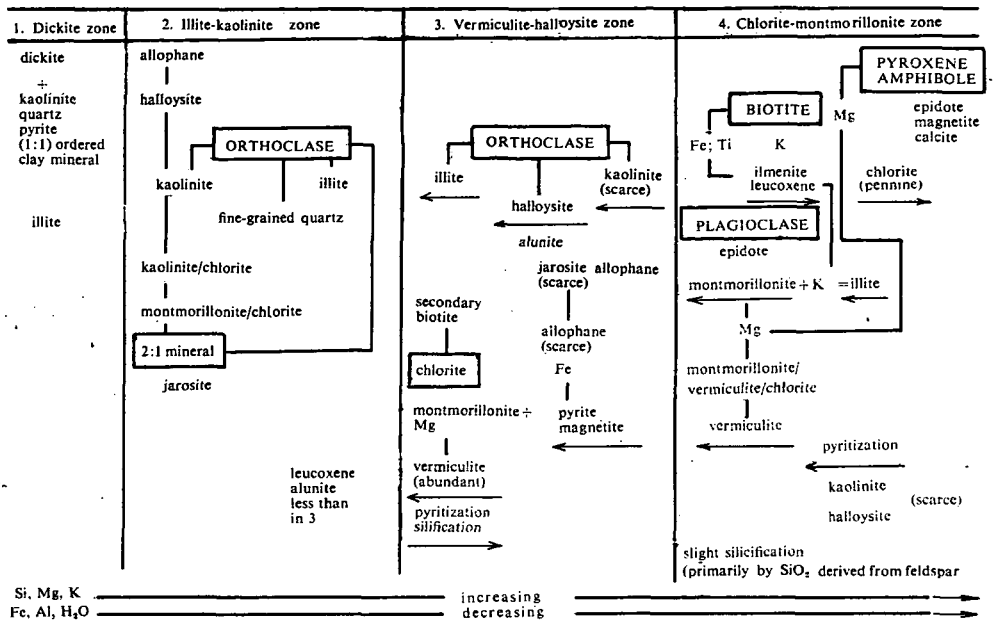


Fig. 1. Equilibria of kaolinite, K-mica and K-feldspar in a coordinate system calibrated in pH ($lg\ OH^-$), $lg\ K^+$ and temperature + pressure (after GARRELS and HOWARD, 1957)

kaolinite in a strip with a width of about 1.5 pH units and a temperature up to 500 °C. From the above the consequence may be drawn that in the simplest case the spatial distribution of the mineral, when advancing toward the lode the K-feldpsar — sericite — kaolin zone follows one after the other. The actual situation is, however, much more complex than that described above, and generally one may distinguish 4 zones among which in that one being next to the lode there is the most kaolinite presenting a very satisfactory crystallization (Table 2).

TABLE 2

Zones of hydrothermal argillization and the mineral decomposition and clay mineral formation processes taking place io them (the authors original compilation)



In the granite of the Velence Mountains in Hungary one may find some zones accompanying the fluorite lodes and containing kaolinite-illite zones which later on pass over into a montmorillonite-chlorite zone.

In the course of the alterations of the volcanic rocks considerably bigger and more interesting hydrothermal deposits were formed in Hungary as compared to the former ones.

Whereas the post-magmatic alteration of intrusive rocks gives rise to rather monotonous clay mineral associations, the hydrothermal argillization of volcanic rocks may lead to the formation of highly differentiated mineral associations. This is due to the typically lower temperatures and pressures prevailing in the process and which, in addition to the formation of pure clay mineral species, also renders possible the formation of phases of a transitional nature. The temperature limit of intrusive and volcanic hydrotherms may — to our mind — be drawn approximately at the $p-t$ conditions of dickite formation. These represent the lowest $p-t$ parameters of the most instrusive processes and the highest ones of most of the volcanic hydrotherms.

The formation of hydrothermal clay minerals in volcanic rocks in Hungary was studied primarily in the Tokaj and Mátra Mts, and to a lesser extent in the Börzsöny Mts as well as in some other scattered localities. On account of both its dimensions and its peculiar mineral associations, it was studied — in particular — the hydrothermal clay mineral formation of Tokaj Mts. The area was studied from geological and depositological point of view by the authors: GY. VARJÚ, T. ZELENKA, G. PANTÓ, E. MÁTYÁS, E. NEMECZ and others.

Hydrothermal argillization of the rhyolite and andesite rocks of the Tokaj Mountains was of a rather great extent mainly on the south-west part and in the Mád—Szerencs basin. The geological setting of argillization consists of a body of acid pyroclastics 300—400 m thick with interbedded and overlying rhyolite-andesite lavas. Hydrothermal argillization is connected with two swarms of faults: one striking NW—SE is very deep, thus the most intense argillization is connected with them. Another swarm which strikes NE—SW is also characterized by a more moderate argillization and by the formation of mainly quartz veins. The Mád—Királyhegy area is a particularly fine example of hydrothermal argillization. The distribution of clay minerals in the vicinity of the lode traversing the Királyhegy is illustrated in *Fig. 2*. The distribution exhibits a characteristic zonality, and the radius of hydrotherm influence is obviously a function of the lithology. The hydrotherms have surged along a fissure that separates a rhyolite lava from some pyroclastics. While the alteration in rhyolite extends, as usual, to some meters only, in that of the much more permeable pyroclastics it reaches many hundred meters. The zone thickness is thus quite considerable and its succession starting outwards the lode is as follows: the central zone is a quartzite and directly next to it we find a kaolinite-dickite zone. This one is highly crystalline and this explains the fact that the Királyhegy kaolinite is not plastic. The kaolinite zone is accompanied by a broad rectorite zone of 140 m width and after that a montmorillonite-illite zone follows.

These succession of zones deviates to a certain extent from the zonality mentioned above in Table 2, since the geochemical setting of Királyhegy is richer in silica and poorer in Mg than the andesite rocks.

In consequence hydrothermal solutions exiting from the lode decompose at the outset the feldspars and the ferrous minerals, taking away the Fe, Ca, Na and K ions. As a results of the ratio increase of the growing SiO_2/Al_2O_3 concentration, conditions for the formation of 3-layer type minerals are given and take place in the rectorite and montmorillonite zones.

Characteristics of the Királyhegy kaolinite, contrary to the Sedlec and Cornwall kaolinites, lay in the fact that their mineral composition is more complex in consequence of which the kaolinite contents of the raw material is low. Another characteristic feature is that kaolinite occurs always together with a considerable quantity of silica which sometimes forms a coherent hard quartz framework besides the always present high quantity of quartz fraction under 1 μm.

This latter one cannot be removed with economic means and is also present in the sedimentary kaolinite of the basin. This kaolinite always contains a relatively high quantity of quartz and thus the Al_2O_3 content of the best industrial qualities does not even surpass 25%. On the other hand, if in the course of ceramic utilization quartz is artifically introduced in the ceramic mass, certain advantages may result from the fact that quartz content of the natural raw material is much finer and thus more reactive chemically than an artificially ground quartz additive. In consequence of the high SiO_2 content, refractory values also increase which can be raised consid-

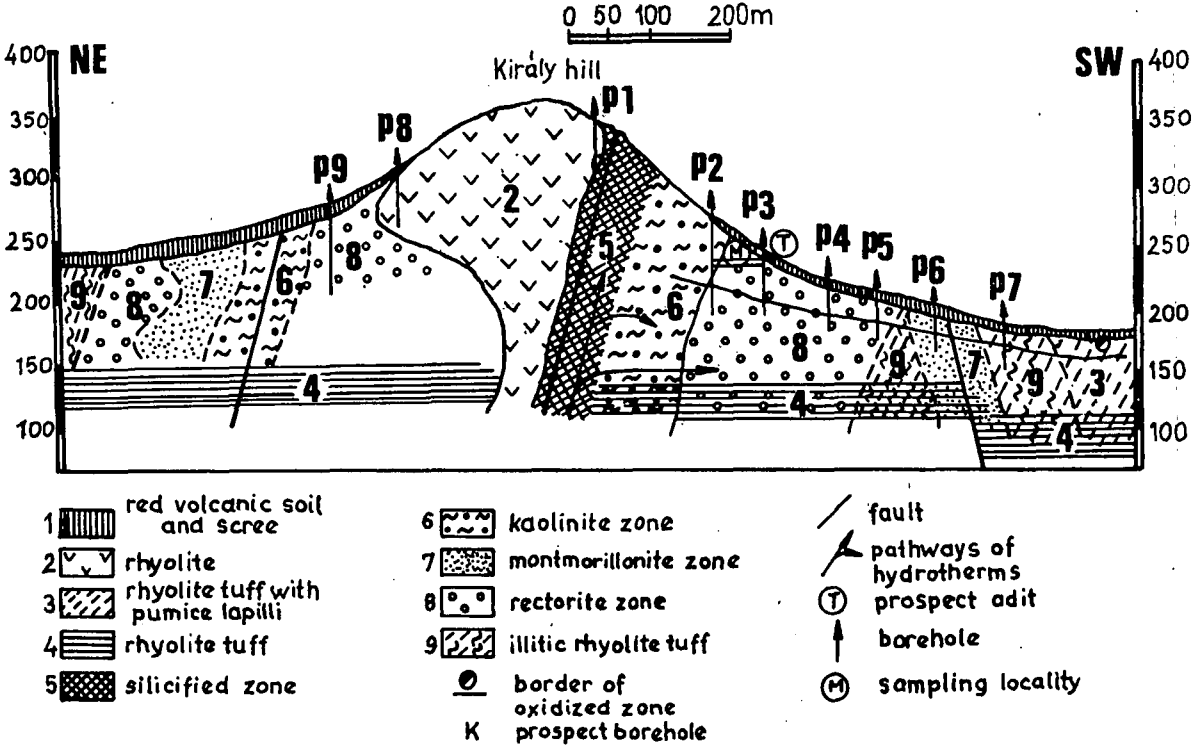


Fig. 2. A northeast-southwest geological profile through Királyhegy, Mád, Hungary (NEMECZ *et al.*, 1963)

erable by special burning of the frequently, encountered alunite mineral present on kaolin deposits, and this increases to a great extent the Al_2O_3 content.

As a final conclusion hydrothermal type kaolin of the Királyhegy deposit may be utilized in manifold ways in the industry, but it appears to be fact that the processing of the raw material requires a very careful preparation.

It is interesting that at Mád and its broader environs, hydrothermal argillization has produced a considerable variety in the kaolinite crystallinity. Next to the foci of hydrothermal activity, kaolinites tend to be highly crystalline with sharp grain outlines, whereas lattice disorder tends to increase away from these foci.

Laboratory evidence has shown that the clay of the Makkosside at Mezőzombor is a remarkably crystalline kaolinite. This same locality has, however, furnished some kaolinite characterized by remarkably weak 001 and 002 reflections, giving X-ray patterns that agree with those of the tubular type kaolinites of Minas Gerais and Les Eyzies. According to axis *b* there is in addition an. expressively irregular mineral, so called kaolinite$_d$ (fireclay) in the kaolinite mines of Szegi which exhibit typically vague reflections in the 4.45—3.76 Å range. Treated with potassium acetat it gives a 14 Å complex that is not destroyed by washing and drying, whereas the highly crystalline Mezőzombor kaolinite is reconverted into a 7 Å mineral almost in consequence of atmospheric humidity. This points to the fact that the Szegi kaolinite$_d$ is a mineral of a highly irregular structure. Likewise such samples are known from the kaolinite mines at Szegi being irregular according to two axes i. e. they contain halloysite minerals. They present that particular feature according to which when ignited on air they are reconverted into kaolinite at a temperature as low as 80—100 °C or when treated hydrothermally at a temperature of 150 °C which goes to prove that they represent structure variations of halloysite being unknown up till now. These variants of regularity at the crystal lattice level may, as shown above, occur within one and the same deposit. Observations at disposal do, however, not permit to give a detailed interpretation of their formation. This complex situation indicates that their irregularity is due to several simultaneous factors.

I should like to point briefly to the fact that hydrothermal kaolinization may occur in andesite rocks too, however, on account of the composition of the mother rock, a more complex clay mineral association is formed in this case. In consequence of the overlapping of the mentioned zones, kaolinite always mixes with illite, expanding clay minerals and chlorite.

Exceptionally, however, kaolin rich deposits may also be formed such as e. .g at Nadap (Velence Mountains), Pilis Mountains but on account of its high pyrite contents, this kaoline is not used for the time being.

According to some of the authors formation of the deposits may exclusively be due to the effect of descending waters. The recognition that most of these kaolinites are of hydrothermal origin too, came much later, but even in the present state so our knowledge we cannot distinguish kaolinites of hydrothermal and supergene origin except by studying the geological conditions. Thus, if the lode wedges out and upwards, the lode fissure peters out in an impermeable formation, the argillization accompanying the lode ceases above the clay mineral; sulphide minerals occurring together with the clay minerals i. e. the clay-mineralized parts are in a close spatial connection with minerals of a hypogene origin such as topaze and pyrite. At Pázmánd (in the Velence Mts) these characteristics together with some others may be considered to be arguments for primary kaolinization. At present prospection of such type of deposits has started in Hungary and may lead to the opening up of new kaolin raw material reserves along with an adequate preparation of same.

No mention will be made of kaolin deposits formed by surface weathering and still existing. They are very well known all over the world. In Hungary, however, such occurrences are not very frequent.

Nevertheless, I should briefly mention some surface weathering products which remained in place and clay minerals of which have been studied in detail.

In conclusion we may state that the Hungarian subaerial clay are dominated by 3-layer type minerals some of which exhibit swelling, and most of which are randomly interlayered. The clay minerals are very poorly ordered. Random stacking is much more pronounced in red than in grey clays. In the red clays iron minerals are in an amorphous state. Typically no crystalline iron mineral can be demonstrated in red clays, and in this respect subaerial clays considerably differ from bauxite iron minerals of which are invariably crystalline and clay minerals of which are mainly kaolinite instead of being of the 3-layer type.

All these conditions of the formation offer explanation for the fact that terrigene clay minerals in Hungary are generally formed in a temperate, whereas bauxites in warm climatic circumstances.

We do know some less important deposits (e. g. Romhány, Petény, Sárisáp) in which redeposited kaolin materials can be found as a result of surface weathering. The original material i. e. its characteristics have changed on account of reworking and transport, their grain size became smaller and of less regular shape. As a result of the above their plasticity increases as well as their raw binding strength; however, their iron content could not decrease to such an extent in order to form a first class raw material.

Now, I intend to give you a short survey on the clay mineral composition of marine sedimentary rocks covering a great part of Hungary. Clastic deposits formed in geosynclines, oceans, inland seas and lagoons, sometimes in considerable thickness, play an important role in Hungary as well as elsewhere.

Some of the authors are in favour of the detritic origin of marine clay minerals ascribing the divergencies in composition to differential settling in sea water. Another group of workers takes sides for the syngenetic transformation of clay mineral and finally the third recent group has proposed the complete and independent synthesis of clay minerals from ions dissolved in sea water.

The endeavour to concert instance of the three above outlined hypotheses of marine clay mineral formation is made difficult by the fact that the authors usually fail to specify any criteria of mineralogical distinction between clay minerals formed in different processes.

Instead of going into the details of these problems, some concrete chaarcteristic examples in Hungary will be quoted.

The Eocene deposits — together with coal-deposits — in the North-Eastern Bakony Mts represent strata formed during strong oscillatory movements, at sites rather close inshore with temporary shoreline displacements. In some profiles in boreholes 500 m deep samples of freshwater and even subareal formations do appear. The approximative ratio of the four groups of clay minerals is given inTable 3. The invariable presence and even dominant amount of kaolinite$_d$ is evident in the vicinity of coal deposits. The abundance of kaolinite$_d$ decreases in the upper layers, but it is important to note that some kaolinite$_d$ remains even above the coal layer and only the layer above it is altogether devoid of kaolinite. This distribution indicates that selective settling has taken place, and also proves that the presence of kaolinite$_d$ in deposits underlying the coal seams ("underclays") is not, as has been assumed, due to a kaolinitizing influence of organic acids. The presence of kaolinite$_d$ indicates a

TABLE 3

Distribution of clay minerals in cores of the Balinka 217 borehole (the number of crosses points to the relative amount of the given miheral)

Depth (m)	Kaolinite$_d$	Illite	Montmorillonite	Interlayered illite/montmorillonite
45.0— 47.0	++	+	++	+
135.6—138.8.	+	+	+++	
364.8—372.8	+	+	anom	+
416.2—426.0	+	+	anom	
442.7—442.8	—	+	—	
443.1—444.0	+	+	anom	
444.2—447.5	+	+	anom	
	Coal, "companion seam"			
445.3—445.9	+	+	anom	
	Coal 1. seam			
448.4—454.0	++	+	—	+
462.05—462.6	+++	++	++	
475.2—478.1	+++++	+	+	+
	Coal			
481.3—483.7	++++	+	—	++

nearshore settling accompanied then by coal formation, too. The strata above are again of the offshore type, as indicated by a transitory increase in the abundance of montmorillonite being able to travel farther in suspension.

Apart from the mineral distribution the changing X-ray pattern of the minerals are also worth noting. One finds that ordering in the clay mineral lattice is low not only in the mineral kaolinite, but even more in the other clay minerals, as a result of detrital structure damage during transport and of irregular cation adsorption.

An additional change of the layers below the coal deposits, especially the dissolution of the minerals contaning iron and the removal of the iron ions—if not deposited as pyrite — is not only a possible but also a very likely process. Just this process makes these deposits suitable to use as supplies of raw materials too, as they contain a refractory clay with a high kaolinite content, which becomes nearly white in the process of calcination.

As compared with the three- or four-layer minerals, the amount of kaolinite is small in the several thousands of meters thick Pannonian deposits and other sedimentary rocks found at great depths in most parts of Hungary. There are two reasons for this. On the one hand, there is the selective settling, as preferably the montmorillonite gets to areas farther from the shore; and on the other, in the strong elecrolyte that is in sea water rather the transformation of the kaolinite present, than is formation is favoured by the diagenetic processes taking place there.

It was intended to give you a short review of the occurrences of kaolinites of different origins in Hungary. As a consequence of intensive mining the stocks of kaolinite have been decreased considerably. Kaolinite has many different uses, most of it is used as filler in paper production and as a raw material of various ceramics.

In the field of ceramics the production of white wares and refractories are the main users. Each of these requires a different quality met by kaolinites of different genetic conditions. This underlines the expansion of the prospecting of kaolinite raw materials. One of the promising but still little studied fields is the prospecting of the primary and secondary deposits formed in the hydrothermal transformation

of acid volcanics. It is evident that these are not identical with the kaolinites formed as residual weathering products of granites. But in view of their high kaolinite content and the presence of other minerals which — like fine quartz — sometimes even favourably affect their use, they are also important raw materials.

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A CLASSIFICATION FOR SEDIMENTARY KAOLINITIC FORMATIONS OF ECONOMIC IMPORTANCE

C. M. BRISTOW

ABSTRACT

A wide range of sedimentary geological formations of which kaolin is a major constituent are used industrially for a wide range of uses, ranging from paper to ceramics. All these formations are of fresh water origin and can be looked at as a continuous series ranging from ball clays with high strength and plasticity at one end of the series to sedimentary kaolins with good powder brightness and rheology at the other end. The changes in commercial characteristics from one end of the series to the other can be related to the mineralogy of the sediments.

In a previous communication [BRISTOW, 1977], the writer discussed the classification of primary kaolin deposits formed in-situ, particularly with regard to the problems of differentiating the effects of weathering and hydrothermal processes in their genesis.

This contribution is aimed at trying to produce a workable classification which is rooted in geological principles for sedimentary kaolinitic formations which are commercially exploited.

In the 1977 paper the following classification of kaolin deposits was proposed: —

Primary	Hydrothermal
	Weathering
	Solfatara
Sedimentary	Kaolinitic Sands
	Sedimentary Kaolins
	Ball Clays

Besides the above named there are also flint clays, fireclays and tonsteins, all of which are kaolinitic materials of sedimentary origin which are used commercially.

The writer believes that it is useful to regard these sedimentary kaolinitic materials as forming three continuous series:

Series 1	Sedimentary Kaolins
	Ball Clays
Series 2	Kaolinitic Sands
	Sedimentary Kaolins

Series 3 (Ball Clays
(
(Fireclays
(
(Flint Clays

Each of these series is continuous and as several types appear in more than one of the series, any clay type may be present in more than one series.

Most clays which have kaolinite as the dominant clay mineral are of fresh water origin, whilst most 'common clays' of marine origin are a mixture of smectite and illite with or without some kaolinite. Of course, only some fresh water clays are of commercial value, the main reasons for not being of commercial value being too high an iron and/or titania content and place value (in an area remote from any area where the clay can be utilised). Other factors such as rheology, particle size distribution and brightness become important for the high value clays such as those used for paper coating and whiteware manufacture and determine whether these clays can be worked in areas remote from centres of consumption.

Series 1

This series comprises most of the non-lithified kaolinitic clays. Nearly all are of Tertiary age.

Five types are quoted in Table 1, taken from well known localities. These could be regarded as 'type localities'.

Type A is the traditional type of coarse particle size sedimentary kaolin as mined in Washington County in Georgia, U. S. A. It is characterised by good brightness, coarse particle size, good rheology and a coarser particle size than the other members of the series.

Type B is the 'North-east' type of sedimentary kaolin, also from Georgia, but generally of a much finer particle size. It is worked as a source of paper coating material.

Type C is an intermediate material between the 'sedimentary kaolins' and the 'ball clays'. It is typified by the refractory clays from the Charente area of the Aquitaine Basin in France.

Type D is the white firing high quality ball clay as typified by the Bovey Basin in Devon, England.

Type E is the highly plastic, very strong ball clay as found in the North Devon (Petrockstow) and Wareham Basins in England.

Below the five types the main characteristics which vary across the series have been listed. The three most fundamental features are the particle size, the crystallinity index and the mineralogy. Chemistry also varies across the series, but not in a regular way and high iron and titania can effectively debar a clay from commercial usage at any point in the series. Organic content does, however, vary in a systematic way, being much higher in ball clays than in sedimentary kaolins largely due to frequent close association with lignites.

The particle size distribution has been commented on by many authors and varies from an *in-situ* below 2 micron content of about 60% for a Type A sedimentary kaolin to about 90% or more for a Type E ball clay. The crystallinity index varies from the relatively well ordered sedimentary kaolins with crystallinity indexes of 0.7 or thereabouts, to thereabouts, to the *b*-axis disordered kaolins which typify most ball clays. The mineralogy also varies in a systematic way with the presence of illite

TABLE 1

	Sedimentary Kaolins			Ball Clays	
	A	B	C	D	E
	Washington County type coarse particle size sedimentary kaolin	N. E. type fine particle size sedimentary kaolin	Charente refractory clay	S. Devon type white firing ball clays of moderate strength and plasticity	N. Devon type ivory firing ball clays of high strength and plasticity
Patricle size:	Coarse				Fine
Crystallinity index:	Well ordered				b-axis disordered
Presence of illite:	V. little or none				Up to 30%
Organic substances:	Rarely present				Present
Modulus:	Low				High
Plasticity:	Poor				High
Viscosity:	Good for paper coating				Poor
Raw Brightness:	High				Low

rising from close to zero in Type A to around 30% in Type E ball clays. The clay fraction quartz content also increases from Type A to Type E.

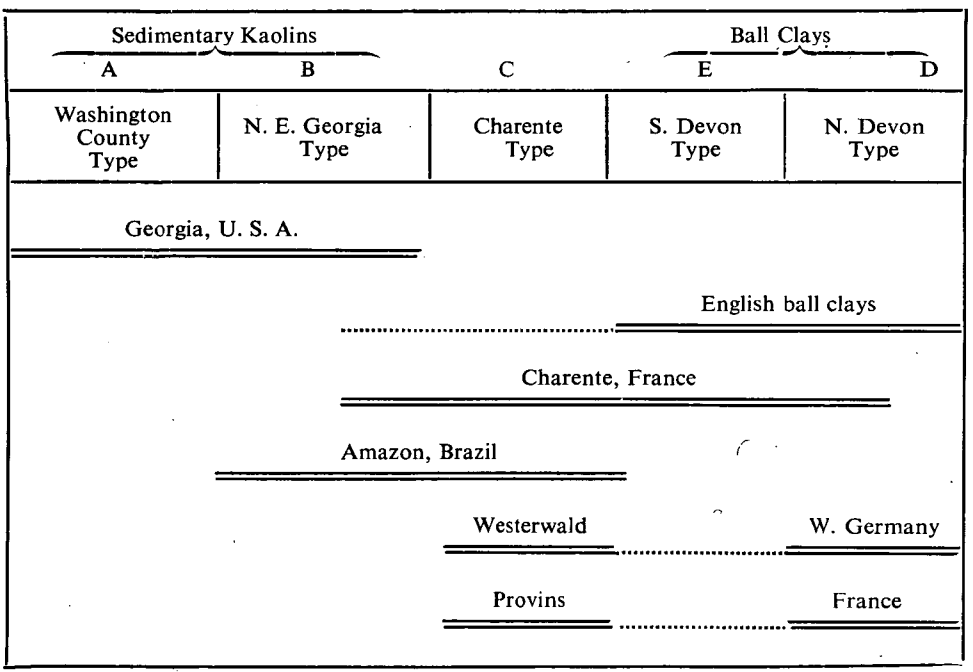
Four commercial parameters are also listed in Table 1, two concerned with paper properties and two with ceramic properties. These are doubtless related to the underlying mineralogy, particle size distribution and crystallinity index.

The ceramic property of modulus of rupture varies from very low strength in the case of sedimentary kaolins to high strength in the case of ball clays. Plasticity also varies in a similar way.

The paper property of viscosity concentration varies in relation to the modulus although in the opposite sense with good viscosity clays being found in Types A and B. Raw brightness varies from the good white clays of Type A to the dark grey or brown ball clays of Type E; this is mainly a function of the higher organic content. Fired brightnesses behave independently of the raw brightness, being mainly dependent on the iron and titania content, which varies in a non-systematic way across the series.

Let us now look at a series of 'provinces' where sedimentary kaolinitic formation occur and see how they can be fitted into this concept:

TABLE 2



Some of the better known occurrences of sedimentary kaolinitic materials are marked on the table with the span of types occurring in each province indicated by a double line for frequent occurrence in the province and a dashed line for infrequent occurrence. By determining the position of the bulk of the clays in a province in the series the approximate commercial characteristics of the materials to be encountered can be inferred.

Series 2

This is a far simple series than the first as the main criterion is the kaolin content, which decreases with increasing sand content. This seems to be a much more polarized series with the bulk of commercially exploited sources lying either in Types A or C. Intermediate types appear to be rare.

TABLE 3

	A	B	C
	Sedimentary Kaolins	Intermediate Types of Sandy Kaolin	Kaolinitic Sands
Kaolin Content:	Over 60%		Less than 20%

The series can run from a type 1D or 1E ball clay through to a kaolinitic sand just as well as with a sedimentary kaolin, although due to the lower value of ball clays in relation to paper clays the refining of kaolinitic sands to produce ball clays is rarely worthwhile.

Examples of kaolinitic sands are the Triassic Hirschau-Schnaittenbach occurrences in West Germany and the Cretaceous occurrences in Cuence and Guadalajara provinces in Spain. Other similar occurrences are found in Poland and Czechoslovakia.

From the literature it would appear that some kaolinitic sands originate as kaolinised arkoses in-situ, whereas others are sediments formed from kaolin and quartz sedimented in that form.

TABLE 4

	A	B	C
	Ball Clays	Fireclays	Flint Clays
Density and Hardness:	Low		High
Plasticity:	Good		Non-slaking

Series 3

This is a simpler series, dependent on a single factor — compaction. If a ball clay is buried to a considerable depth and subjected to compaction it will first be converted into a fireclay and then into a flint clay. Whereas a ball clay is soft and plastic and is readily slaked into water, a flint clay is hard, dense and non-plastic [KELLER, 1976]. The microscopic texture of flint clays, as seen under the S. E. M. is indicative of pressure having reduced the porosity so that the crystals of kaolinite are interlocked in such a way that the external crystal form of kaolinite is rarely displayed.

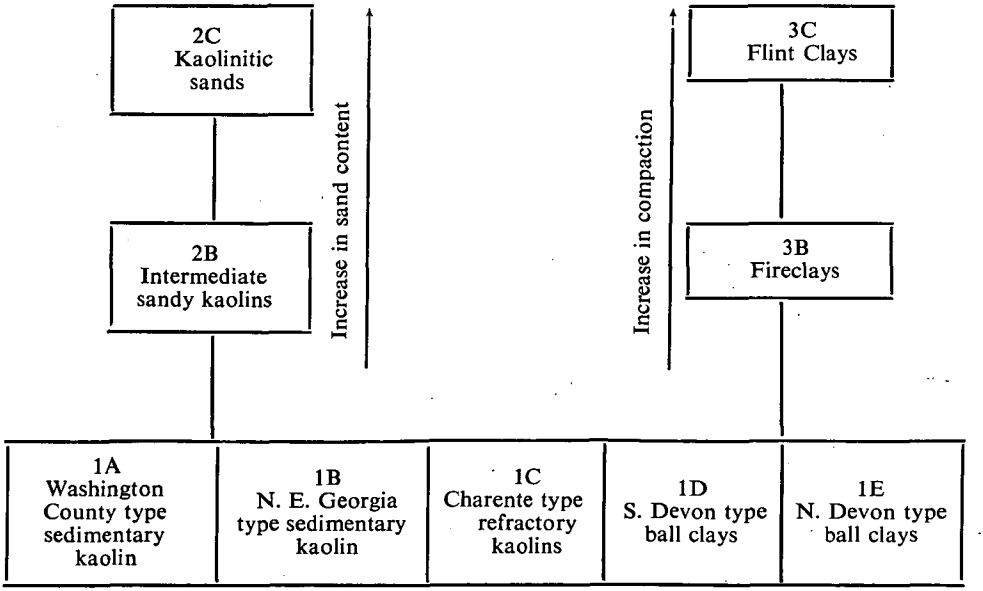
It is not without significance that whereas nearly all ball clays are of Tertiary age, fireclays and flint clays are generally of Palaeozoic age indicating the effects of greater compaction due to deeper burial and/or a greater length of period of burial.

It ought to be mentioned that the term 'fireclay' appears to have a different usage in different countries. The term is of Anglo-Saxon origin and refers to the clays found in association with the Coal Measures of Upper Palaeozoic age in Britain and the eastern United States. Because the type of kaolinite in fireclays is characteristic (*b*-axis disordered), the term 'fireclay kaolinite' began to be used. Subsequently it was found that most ball clays contained the same type of kaolinite. In Germany this had the unfortunate results that any clay which was used for refractory purposes and contained *b*-axis disordered kaolinite came to be called a 'fireclay', at least in commercial circles. This includes a lot of material which most British geologist, would call 'ball clay'. Tonsteins are, of course, a completely different type of clays originating from material of volcanic origin, so cannot be fitted into this classification.

Whilst this series originates from the ball clay end of Series 1; there ought to be an analogous series extending from sedimentary kaolins through to more compacted analogues to fireclays and flint clays. As far as the writer aware no such analogues have been discovered, but it would be very interesting if such a series could be discovered.

The three series are summarised in the following diagram:

TABLE 5



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KAOLINIZATION PROCESSES IN AN AREA OF SEGOVIA (SPAIN)

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ABSTRACT

In Vegas de Matute, South of Segovia, there is a kaolin deposit formed by weathering on Hercynian gneisses of the Spanish Central Massif, fossilized by the overlying Albian, which is also kaolinitic (sands and clays).

Mineralogical differences (clay and heavy minerals) and differences in kaolinite crystallinity make it possible to distinguish between both types of kaolin (residual and sedimentary), even though the Albian kaolinitic sands are derived from the erosion of residual kaolins formed on acid rocks of the Central Massif, such as those fossilized in this deposit.

Most of residual kaolin was probably eroded prior to Cretaceous times and the remaining kaolin was preserved as a deep crust because of poor drainage. The weathering profile is dominantly kaolinite near the top with the smectite content increasing with depth to a maximum of 60%. Sometime after the Cretaceous period some of the Albian kaolin was altered, in a basic environment, to smectite.

INTRODUCTION

Kaolin deposits formed "in situ" on silicic rocks by weathering processes are very limited in Spain, in spite of the fact that silicic rocks occupy a large portion of Western Spain. These extensive granitic and gneissic areas have supplied, during different geological ages, kaolinized materials that have given rise to kaolinitic sediments and at times to sedimentary kaolin deposits, proof that time after time these residual kaolinized rocks were eroded; however, at present several meters thick kaolinized weathering crusts can rarely be found.

The example given in this paper demonstrates the existence of a post-Hercynian stage of kaolinization on metamorphic rocks of acid character, which have been eroded to a great extent, but whose lowest levels have been preserved because of the overlapping of Cretaceous sediments. These sediments are kaolinitic in composition and are, ipso facto, the result of the dismantling of the kaolin crusts developed on those areas during the same period.

The Cretaceous kaolin facies (Weald and Utrillas, Lower Cretaceous and Albian, respectively), is widespread in Spain, with important deposits of kaolinitic sands in the Iberian Range (Cordillera Ibérica). However, these sands don't overlap the source area itself.

GEOLOGY

The deposit of Vegas de Matute is some 25 km south-east of the capital, Segovia. From a geological point of view, it is located in the narrow Mesozoic strip that borders to the north the larger part of the Spanish Central System *(Fig. 1)*. The Central

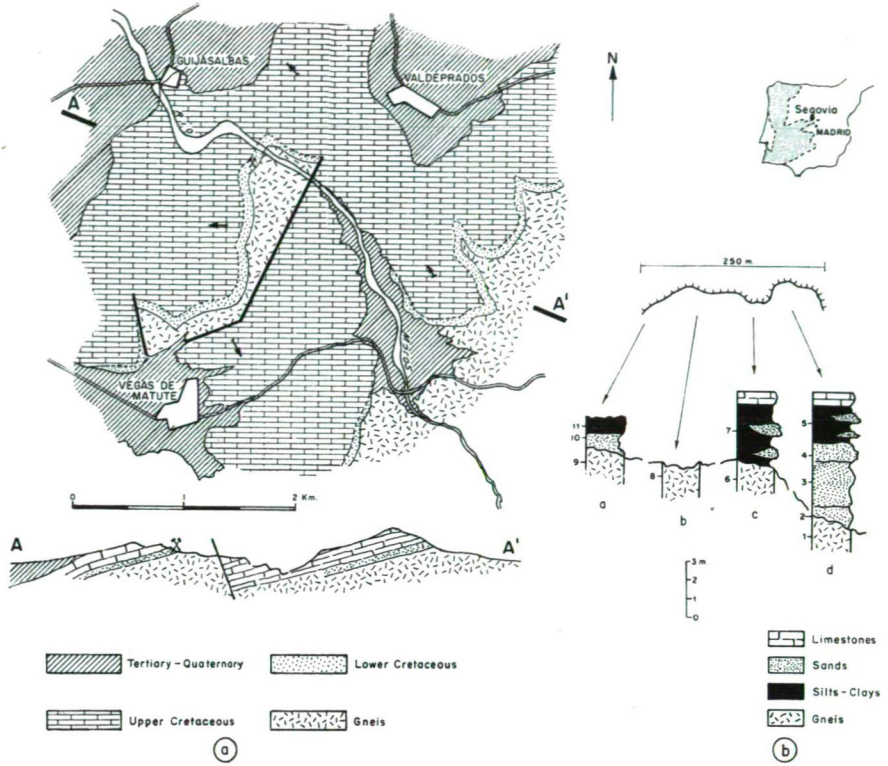

Fig. 1. The Vegas de Matute area (Segovia, Spain)
a) Cartography of the studied area and location of the kaolin deposit
b) Different sections along the kaolin deposit and sampling location

Massif is formed by metamorphic and plutonic rocks that extends eastward from the Portuguese frontier to the Iberian Range. The meridional and septentrional limits of the Central System are formed by Mesozoic and Tertiary materials that constitute the basins of the Tajo and Duero rivers, respectively. This kaolin deposit is located in the central part of the afore-mentioned mountainous range. The principal characteristic of this sector is its petrographic uniformity as well as the degree of metamorphism. The Central Massif is formed almost exclusively by catazonal gneisses, the 90% of which is of an 'augen' type, with large phenocrysts of potassium feldspar, and the rest corresponds to fine grained banded gneisses and gneisses with plagioclases interlayered in an 'augen' formation.

The gneisses were derived from pre-Ordovician rocks, which probably orginated during the Cambrian period. The metamorphic process that gave rise to these rocks belongs to the Hercynian and demonstrates characteristics which are similar to the intermediate type formed under low pressure conditions [MIYASHIRO, 1972]. A detailed study of the metamorphic rocks of the Central System [LÓPEZ RUIZ, *et al.*, 1975], enables one to observe, however, important variations in time and space as regards the metamorphism of this region, which lends support to the hypothesis of a plurifacial and polyphase metamorphism.

A Mesozoic and Tertiary cover is found on this crystalline substratum, bordering the entire Spanish Central System.

The Mesozoic lies above the gneisses, fossilizing an important paleo-relief, which explains why its thickness varies notably from one sector to another. Furthermore, the basement – in its uppermost part, represents an alteration which normlaly reaches a depth of 2 or 3 meters.

The Mesozoic cover is limited exclusively to the Cretaceous. The Cretaceous series consists in its lower part of detrial sediments (sands, silts and clays of a kaolinitic nature), whose thickness can attain up to 50 meters, although generally it is less. Compared to other areas, the detrital levels are considered to be from the Albian period. These detrital sediments resemble facies similar to fluvial and lacustrine environments. On the altered gneisses of the Vegas de Matute deposit there are detrital beds, with thicknesses not exceeding 8 meters. These are Albian layers which together with the altered gneiss, are exploited for kaolin. In the mine it is possible to observe how these detrital facies change frequently and abruptly in thickness and lithology *(Fig. 1b)*, as it is generally in the case of the Albian sediments of this area bordering the Central System.

A succession of Upper Cretaceous (Cenomanian-Turonian) limestones and marls overlies the detrital beds. More recent Mesozoic sediments than those described above are absent in this region.

Lastly, and also forming parts of the cover are Paleogene and Neogene sediments, which partially overlie the Cretaceous or the gneissic substratum. The Tertiary, exclusively continental in origin, comprises coarse detrital sediments in the lower portion, and sandy or clayey sediments in the upper portion. These materials thicken considerably toward the north.

The Hercynian orogenesis is not only responsible for the metamorphism that affected and originated the gneissic substratum, but it also produced the intense fracturing of the Paleozoic materials and plutonic rocks of the Central System. The Mesozoic-Tertiary cover was gently folded during the Alpine orogeny. The Alpine activity caused subsequent displacements and in some cases produced fracturing of the substratum, wherein the cover adapted itself to the movement or relief on the basement.

MATERIALS AND METHODS

The Vegas de Matute deposit has been sporadically mined. Its location is shown on the map in *Fig. 1a*. The open cut of the mine was sampled in detail and the sequence of materials established. Other profiles were also sampled outside of the active open-pit mine. The characteristics of these series and the sampling positions are shown in *Fig. 1b*.

The lack of lateral continuity of the detrital beds is to be noted; there is alternate overlapping, reflecting an enormous variation in granulometry (silt, sands, silty-clays, etc...), but the kaolinitic character is constant in every case.

A residuum of white clay is found occasionally with a thickness of 1 m on the altered gneisses which contains sandy ferruginous nodules with a diameter between 2 and 5 cms surrounded by a coating, like an aureole, of white clay.

These materials were studied by means of X-ray diffraction, petrographic microscopy, electron microscopy, and chemical analysis.

ANALYTICAL RESULTS

From the results of the mineralogical and chemical analyses, together with polytype determinations of the kaolinites of the different samples studied, (Tables 1, 2 and 3, and *Fig. 2*), it can be deduced that two types of materials exist:

a) More or less altered metamorphic materials, with variable content of feldspars, smectite and kaolinite, whose polytype varies from pM-T to T. Heavy minerals are present including zircon and tourmaline.

b) Sand and silt beds, rich in kaolinite and with variable content of anatase, goethite and hematite, and practically free of feldspars. Kaolinite in these materials represents disordered polytypes, fundamentally pM or pM partially ordered. The suite of heavy minerals is highly complex.

TABLE 1

Mineralogical composition (total)

Samples	q	c. m.	f	Others
1	60	25	15	—
2	40	60	—	—
3	60	40	—	—
4	>95	5	—	—
5	50	50	—	Anatase
6	50	20	30	—
7	85	15	—	Anatase
8	55	45	—	—
9	65	35	—	Goethite
10	90	5	—	Goet.-Hem.
11	70	30	—	Goethite

c. m. = clay min.; q = quartz; f = feldspars

TABLE 2

Mineralogical composition (< 10 μm frac.)

Samples	q	k	m	mo	Others	K. polyt.	H. In.
1	5	60	5	30	—	pM-T	0.54
2	20	75	<5	5	—	T	1.1
3	30	50	<5	>15	—	pM	n. d.
4	15	85	tr	tr	Goet	pM	n. d.
5	10	90	tr	—	Anat.	pM	0.36
6	10	25	10	55	—	pM-T	0.50
7	10	90	tr	—	Anat.	pM	0.28
8	20	75	<5	5	—	T	1.01
9	5	>90	<5	tr	Goet.	pM-T	0.55
10	25	50	—	10	Goet-Hem (15)	pM	n. d.
11	25	60	—	15	Goet.	pM	0.35

q = quartz; k = kaolinite; m = micas; mo = montmorillonite; k. polyt. = kaolinite polytype; H. In. = Hinkley Index

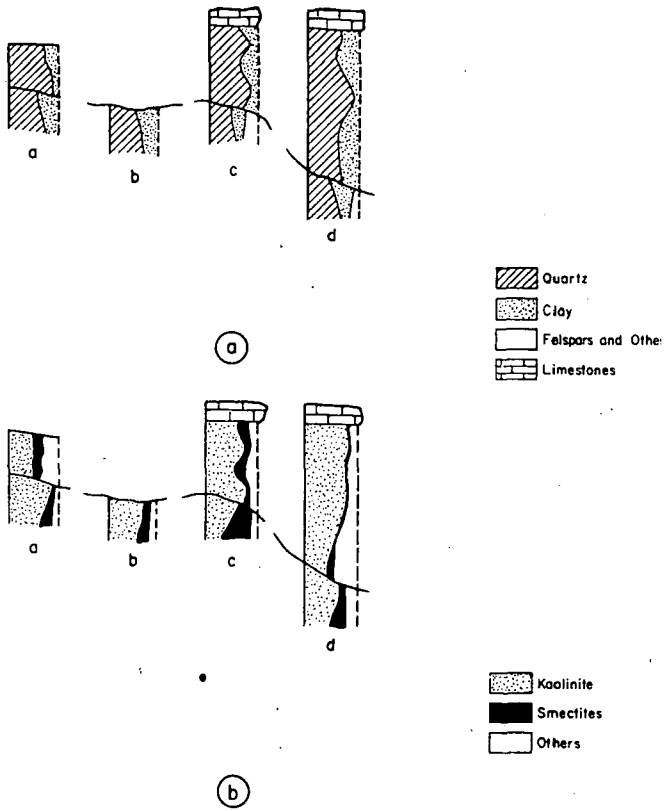

Fig. 2. Mineralogy of the kaolinized gneisses
a) $<10\ \mu m$ fraction b) total sample c. m. = clay minerals; q = quartz; f = feldspars; k = kaolinite; mo = montmorillonite; sam = sample number (see *Fig. 1b*)

The quantitative mineralogical analyses of these samples corresponding to temamorphic materials are represented graphically in *Figures 3a* and *3b;* said figures correspond to the less than 10 micron fraction and the total sample, respectively. In the first of the figures it can be observed that the content of non-clay minerals is clearly related to the degree of alteration which these materials have undergone, the alteration decreasing with depth. On the other hand, it can also be observed that the kaolinite and feldspar content is inversely related to each other, which is similar to that corresponding to kaolinite and smectite.

The attempt to correlate, graphically, the results of the quantitative mineralogical analyses of the samples belonging to the second type of materials is negative. This is because the materials in question present different granulometric characteristics and are distributed in a lenticular fashion throughout the entire sampled outcrop.

Data of particular interest are the absence of feldspars and the presence of heavy minerals not observed in underlying materials. The suite of heavy minerals most frequently observed were tourmaline, zircon, andalusite, staurolite, kyanite and rutile, and infrequently garnets, brookite and topaz.

With regard to the white clay beds with ferruginous nodules, the high content of well crystallized smectite (30%—50%) is to be noted, (Biscaye index), which represents an anomaly in the composition of the Albian materials of this region. The nodules contain about 30% smectite, while the matrix of the surrounding sediments contains as much as 60%. The iron content increases towards the interior of the modules, so that the aureole or crown appears white (1.38% Fe_2O_3) whereas the interior is red (3.70% Fe_2O_3).

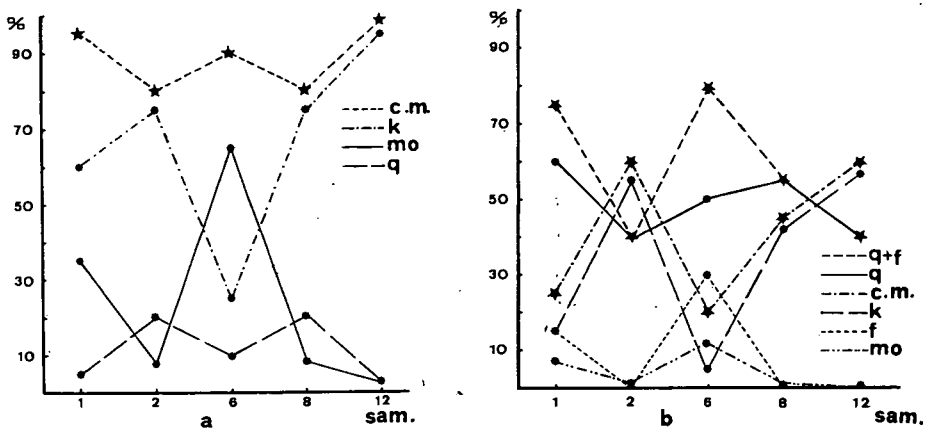

Fig. 3. Mineralogical composition of
a) total sample
b) $\leq$10 μm fraction in the same profiles as in *Fig. 1b*

TABLE 3

Chemical analyses (< 10 μm frac.)

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	L. Ign.
1	57.30	32.61	0.47	0.01	0.19	0.20	2.50	5.35
2	56.28	31.90	1.00	0.03	0.13	0.90	0.52	9.04
3	57.25	36.50	0.48	0.18	0.25	1.60	0.36	3.10
4	55.29	37.06	0.60	0.28	0.33	0.32	0.76	5.16
5	50.39	35.70	0.70	0.42	0.19	0.11	0.67	11.73
6	52.65	33.27	0.52	0.25	0.54	0.26	2.11	10.30
7	49.37	36.41	0.64	0.12	0.26	0.34	0.43	12.25
8	50.48	35.69	0.40	0.14	0.26	0.29	0.67	11.99
9	49.92	37.21	1.66	0.09	0.23	0.17	0.38	10.21
10	51.60	35.23	3.20	0.50	0.41	0.12	0.96	7.87
11	49.46	33.65	1.84	0.25	0.39	0.06	0.95	12.37
Fe-Nodule	54.94	28.50	3.70	0.17	0.27	0.60	0.13	10.80
Matrix	55.02	29.20	1.38	0.26	0.27	1.00	0.22	12.58

DISCUSSION OF RESULTS

Subsequent to the Hercynian metamorphism of the region, in the area studied, two fundamental geological processes independent of each other took place. The first was the alteration of granites and gneisses by weathering processes which resulted in profiles *(Fig. 2* and *3)* with kaolinite dominant in the upper portion and

smectite increasing in content toward the base up to a maximum of 60 percent. The second event was the erosion, transport, and deposition of the weathered crust resulting in Albian kaolinite sands, silts, and clays (Utrillas facies) in whuch the kaolinite is clearly an inherited mineral [LÓPEZ AGUAYO and MARTÍN VIVALDI, 1973].

The samples of the weathering crust were collected with reference to the gneissic surface and one can assume that they correspond to non-eroded crusts where drainage was deficient because the smectite content could be as much as 30 percent higher in the thin crust.

The weathering process affected micas, biotite, muscovite, feldspars and chlorite, and it was of a regional character [GALÁN and MARTÍN VIVALDI, 1975].

The Utrillas facies of the Albian are kaolinite sands alternating with silt and clay layers. The kaolinite in these sediments is inherited from the weathering crust and their genesis has been studied extensively by LÓPEZ AGUAYO and MARTÍN VIVALDI [1973], GALÁN *et al.*, [1975], and LÓPEZ AGUAYO *et al.*, [1971]. The kaolinite in the weathering crust is a well ordered type or only slightly disordered (T...pM-T) with particles ranging in size between 0.1 and 0.5 micrometers. In the Albian beds the kaolinite is disordered with particle size of less than 0.1 micron. SHUTOV *et al.*, [1966] and LÓPEZ AGUAYO and MARTÍN VIVALDI [1973] have indicated that transport processes disorder kaolinites. This present study shows that the kaolinite in the weathering crust is ordered and after erosion, transport and deposition in the Albian the kaolinite is disordered.

The heavy mineral suite of the weathering crust and the Albian beds also differ. In the weathering crust zircon and tourmaline are found, whereas in the Albian beds the suite is more complex with zircon, tourmaline, andalusite, kyanite and rutile common and with occasional grains of staurolite, garnet, brookite, and topaz also present. This indicates that the source area includes more than the weathering crust on the granites and gneisses in the immediate vicinity.

Another interesting point in the area studied is the occurrence and composition of the ferruginous nodules in the silt matrix in the Utrilla facies. From field observations these nodules are syngenetic and are interpreted as "armoured mud balls". The composition of these nodules is different from the silt, so the smectite content in their centre is much less than the smectite content of the silt matrix. It is suggested that much of the disordered kaolin in the silt matrix was altered to smectite after deposition by ground water percolation which had a basic pH. The ferruginous nodules were not attached in the interior but only the outer white skin was leached. It is also suggested that the circulating ground water and not only the transport could contribute to the disordering of the kaolinite, because the Albian kaolinites of the Iberian Range which are much further from its source area are characterized by a high cystallinity [GALÁN, 1976], may be because they don't overlap rocks of poor drainage like in this case.

CONCLUSIONS

i The kaolinites in the weathering crust and in the Albian sediments differ in crystallinity. In the weathering crust the kaolinite has a higher crystallinity and coarser in particle size. This difference is attributed to transportation and deposition because it is believed that the Albian kaolinite was derived from the weathering crust.

ii Some silt beds in the Albian contain ferruginous nodules and the clay in the interior of the nodules contains less smectite then that found in the surrounding

matrix. It is suggested that high pH ground water movement through these silt beds altered some of the kaolinite to smectite and contributed to the disordering of the kaolinite although the fossilized weathering crust also contains increasing amounts of smectite toward the gneissic surface due to a deficient drainage.

iii This study of a localized area indicates that a weathering crust was locally preserved and that the kaolinites in the Albian sediments were derived from the weathering crust. A wider area should be studied to shed additional information on this problem of kaolin genesis of the Spanish Central Massif and the associated kaolinitic sediments.

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KAOLINIZATION BY CIRCULATING SURFACE—WATER IN THE UPPER PART OF INTRUSIONS

P. WIEDEN

The author postulated in 1978 in the paper "Genesis and Age of Kaolin Deposits in Austria", that besides the normal weathering agents circulating ground water with variation in pH, redox potential resp. and mineralization is due for the building of clay minerals (kaolinite and montmorillonite).

H. SCHRÖCKE [1978] indicates in the publication "Geotektonik und Lagerstättenbildung", that one can explain hydrothermal reactions by a system of convection of ground water streams rising round the intrusives. The source of energy is the capacity of heat of the magma.

A hydrodynamic model [J. CATHLE and D. NORTON, 1974] — 2 km diameter of the pluton, top in 2.75 km depth — shows, that at a difference of temperature of

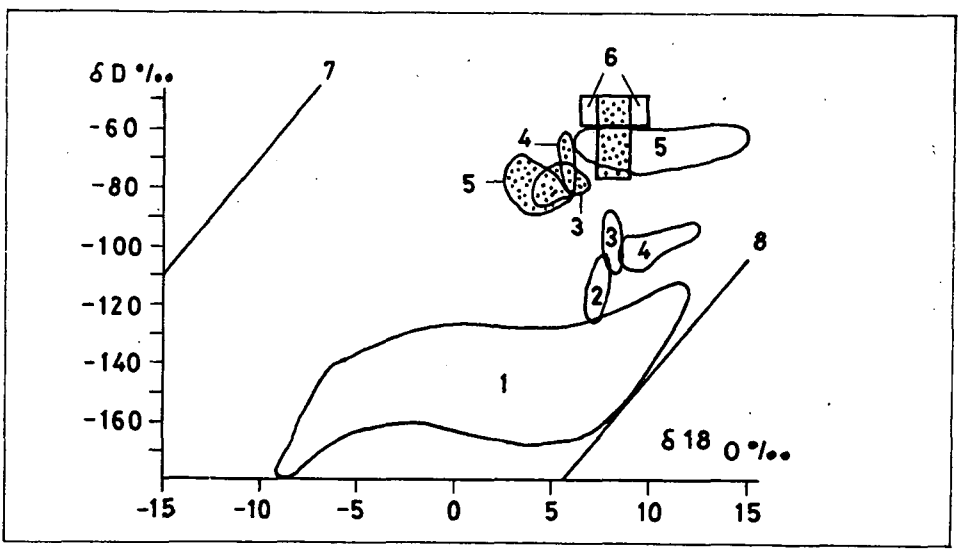

Fig. 1. O- and H-isotope ratios of clay minerals, biotite and sericite. SHEPPARD, NIELSON and TAYLOR [1971]
The isotope ratios of H and O of biotite, sericite (dotted) and clay minerals (white) from transformed rocks of the deposits Butte = 1, Climax = 2, Bingham = 3, Ely = 4, Santa Rita = 5. Hydrothermal water in equilibrium with biotites (calculated) of Bingham, Ely and Santa Rita = 6, area for magmatic water thick dotted. Composition for the surface water = 7, for O and H kaolinite in equilibrium with the surface water = 8.

700 °C against the neighbouring rocks convection streams of the pore water must be come about.

If the magmatic rocks have a permeability of 0,15 md (millidarcy) and the neighbouring rocks have a permeability of 0,30 md, in the time of cooling of the pluton in the range of 10^5 years until 20% of the starting temperature, there are 100 circulations.

The amount of water which goes through the upper part of the pluton is three times more than the mass running through the rock. The flow speed is about 30 m/year.

Hydrogen and oxigen isotope content of the layer-silicates of most of the porphyric copper ore deposits [S. SHEPPARD, 1969, 1971] lie in the D-^{18}O diagram between the streight line of the surface water and the streight line of the kaolin being in equilibrium. Sericite and clay minerals (kaolinite, montmorillonite) have D- and ^{18}O-values correspondig of today's rhythm of the surface water *(Fig. 1* and *2)*.

By intrusion into a sufficiently permeable neighbouring rock system a mechanism of convection starts, bringing cold surface water downwards *(Fig. 3)*.

As a result of cooling of the pluton or batholith follows the fissuring (thermal cracking). Depending on temperature, pH, Eh and the primary chemism of the parent

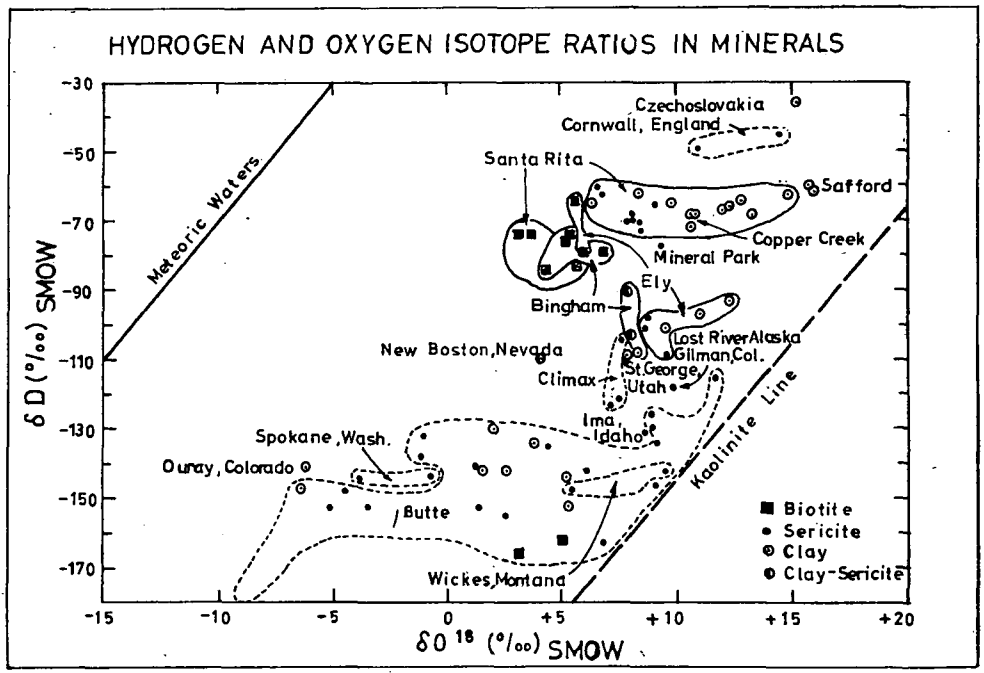

Fig. 2. O- and H-isotope ratios of clay minerals (several deposits, ČSSR and Cornwall). SHEPPARD, S. *et al.*, [1971]
Plot of D verus O^{18} for all the biotites and sericites analyzed in this study and for Butte by SHEPPARD and TAYLOR [1970]. Data for hypogene clays from porphyry copper deposits of the USA [SNT, 1969] and a dickite from Horni Slavkov, Czechoslovakia [SAVIN and EPSTEIN, 1970] are also included. The meteoric water line [CRAIG, 1961] and kaolinite line [SAVIN and EPSTEIN, 1970] are given for reference.

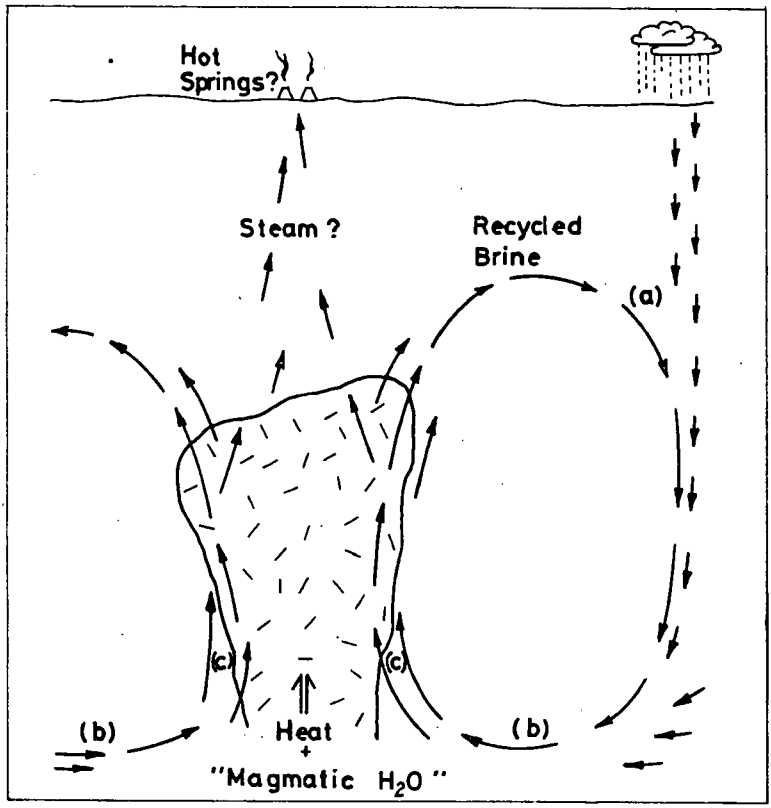

Fig. 3. Schematic cross-section of a porphyry copperstock, showing its postulated interaction and effect on groundwater circulation, in those situations where abundant argillic alteration has taken place. SHEPPARD, S. *et al.*, [1971]

rocks, kaolinite resp. other clay minerals are built by ascendent or descendent conditions. Mixed types are probably built, where surface water, magmatic water resp. pore water and reaction water (from OH of silicates) are participating.

SUMMARY

The formation of a deposit of kaolin is possible if following conditions are realized.

1. The rocks (granites, gneisses, granulites, porphyrites, trachytes, andesites etc.) must have the primary petrographic composition for building kaolinite, dickite, halloysite and other clay minerals.
2. It must be a tectonic or thermal fissuring to produce a sufficient permeability to allow a circulation of solutions.
3. These solutions must have a pH-value of ~ 7, a corresponding Eh-value, may or may not contain organic substances (?) and must have such a temperature, that in a certain time the reactions are going on to form a reasonable deposit of kaolin.

4. The kaolin must be protected by sedimentary overburden or by tectonical sinking. Now it is to be proved which possibility for the genesis of a deposit is actual.
   a) "Weathering" in the classical sense. Influence of organic material (humic and fulvic acids), bleaching and climatic factors.
   b) Convection of surface water and parts of magmatic water influenced by a "hot-spot" of a pluton.
   c) Hydrothermal origin in connection with volcanism.
   d) Mixed-type.

REMARK

The definition whether a deposit is of a weathering, a hydrothermal or of a mixed type depends on the low or high grade of investigation. So it is necessary to do more geological-mineralogical work and give more attention to the "tiny" minerals, which are mostly overlocked. Clay minerals are not so attractive as ore minerals. On the other hand we have to do more investigations in geochemical and isotope direction.

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FIRECLAY AND KAOLIN DEPOSITS IN ROMANIA

G. NEACŞU and VASILICA NEACŞU

ABSTRACT

The fireclays in Romania are in general high-graded as regards their refractoriness, and are the most frequently connected with the Lower Liassic formation and more rarely with Pliocene deposits.

The main kaolin deposits are originated through hydrothermal alteration of some Tertiary rocks and by transport and sedimentation under continental-lacustrine conditions of kaolinitic sands and/or clays, resulting from reworking of some old weathering crusts.

The exogenic residual deposits are less important, being represented only by relics of fossil weathering crusts.

The Romanian kaolins are very seldom utilizable as raw material for industrial purposes; generally they are utilizable after washing and/or chemical treatments.

INTRODUCTION

Fireclay and kaolin deposits of Romania are characterized by a large genetic and facial variability, are covering a long age interval and are widespread in about all the country.

Hydrothermal kaolins are especially connected with Tertiary effusive rocks of East Carpathians and Apuseni Mountains, relics of old kaolinitic weathering crusts are recognized in Baia Mare area or in South Carpathians, continental sedimentary deposits of weakly coherent sands and clays are located in Dobrogea, Transylvania and Banat, tightly coherent kaolinitic clays (refractory clays) are well developed in Apuseni Mountains and South Carpathians; the last ones are transformed into pyrophyllitic schists.

The shape of the kaolin-bearing deposits are quite various: beds, lenticular beds, lenses and pockets for sedimentary kaolin deposits, and irregular bodies or zones, veins, dykes and sills for hydrothermal kaolins.

The kaolins from the weathering zone, which are considered as the most important for exploitation, are frequently high-grade materials.

The main kaolin-bearing deposits mined in Romania are the hydrothermally kaolinized rocks from Harghita and Parva, the sedimentary kaolinitic sands and clays from Aghireş, and Medgidia, and the fireclays from Suncuiuş and Schela-Viezuroiu. The Schela-Viezuroiu fireclays are wrongly called refractory clays; in fact these are pyrophyllitic schists with refractory qualities. An improper name is used for Harghita kaolin to (as commercial product), constituted mostly of hydromica.

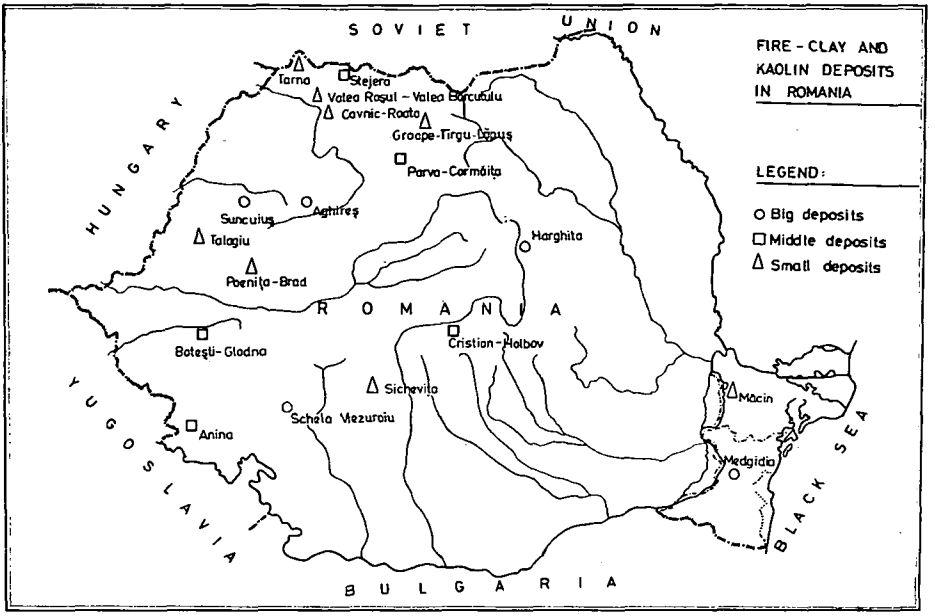

Fig. 1.

FIRECLAYS

Suncuiuş. The most important refractory clay deposits of Romania are located within Apuseni Mountains, Pădurea Craiului Massif.

The thickness of the Lower Liassic Gresten Formation with fireclay deposits varies between 40—100 m and it is represented by a complex of coarse sandstones and conglomerates with clayey, frequently refractory intercalations (bed-lenses). The productive horizon is formed by red clays encompassing intercalations and lenses of calcareous conglomerates and breccia in the basis, and sandy limestones, in the top of the horizon. Areas of repartition of refractory clays covers 120 km^2. A number of 15 fireclay levels are to be considered; their shapes are lenses and lenticular beds, ranging from 0.2 to 15 m in thickness, and extending laterally over hundred metres. The Suncuiuş fire-clay deposits are mined for a minimum thickness of 0.2 m and a refractoriness exceeding 169 PI.

Mineralogical composition of clay fraction is dominated by kaolinite T with subsidiary illite and quartz. Illite contents increase in nonrefractory clays, reaching to 20—40%, and kaolinite pM occurs usually within carbonaceous clays. Hydrargillite, montmorillonite, dickite, nacrite (along fissures in association with pyrites, sericite, chlorite and melanterite generated by pyrite oxidation), goethite, hematite and siderite have been incidentally recognized. Among heavy minerals there are recognized tourmaline, magnetite, ilmenite, zircon, rutile, staurolite and garnets.

The beneficiation tests carried out by washing of nonrefractory clays led to the result that 54% of the washed clay has a refractoriness of 171—173 PI; concomitantly the plasticity and compression strength increase to 22% and 50%, respectively.

Anina. The refractory clay deposits of Anina are associated with important pit coal deposits. These deposits (coal and fireclays) are mined underground up to 900 m depth.

The fireclay and pit coal bearing formation represents the Lower Liassic Gresten facies of the Semenic Unit; it is conformably overlain by a bituminous shale horizon and is overlying unconformably the red gritty deposits of the Lower Permian. The productive complex, so-called "coaly horizon", located in the southern limb of the Anina anticline is 250 m thick and consists of micaceous clayey sandstones, coaly shales, coals and fire-clays (2 beds). The tectonic framework of the area is characterized by important faults with clips up to 600 m which are dividing these clay and coal deposits into numerous blocks.

The mineralogical composition of the clay fraction is dominated by kaolinite; there also occur illite, quartz and small amounts of feldspars, iron oxides and hydroxides, carbonaceous matter. The kaolinite shows a crystallinity Hinckley index of 1.3—1.5 (T variety) for 70% of samples and 0.8—1.2 (pM and M varieties) for the remaining 30% of samples. Concomitantly with the increase of the tectonic pressure, pM and M varieties turn into kaolinite T.

Cristian and Holbav. In the vicinity of Cristian locality, two parallel synclines include Lower Liassic deposits containing refractory clays. The productive formation consists of sandstones, clayey breccia, clayey-coaly shales, coal and refractory clays; they are unconformable overlying the Anisian limestones and support the Carinian. In the Joedere Valley are 5 fireclay layers and in the Poiana Poienița 9, layers of 0.8—2 m thickness are encountered.

In the Holbav locality area, the fireclays are included in a coal-bearing clayey-gritty formation. There are 5 fireclay beds (up to 2 m thick) intercalated within the productive complex.

Mineralogical composition of Cristian and Holbav fireclays consist in kaolinite, illite, quartz, feldspars and sporadically pyrite, siderite, hematite.

Like at the Anina fireclays, the exploitation is carried out underground and presents difficulties due to tectonic causes.

Boteşti-Gladna. The refractory clay deposits of Boteşti-Gladna area consist in a few layers of 2—4 m thickness included in the Pannonian sandy-clayey sequence of the Caransebeş Basin.

Mineralogical composition of the Boteşti-Gladna fireclays consists in kaolinite (50—60%), illite (20—40%), montmorillonite (0—20%), quartz (5—30%), feldspars (0—5%), iron oxides and hydroxides. Refractoriness ranges from 155 to 171 PI.

Concerning their economic value these deposits present a reduced importance.

WEAKLY METAMORPHOSED FIRECLAYS

Schela-Viezuroiu. The geological framework of Schela-Viezuroiu area is represented by the Danubian Autochtonous, built up in this region by Suşița granite, Schela formation (sedimentary rocks with fireclay, weakly metamorphosed) and sedimentary rocks of Sarmatian age.

The fireclay-bearing complex is represented by Schela formation, which includes pyrophyllitic schists with intercalations of quartzitic sandstones and microconglomerates. The productive horizon, 140 m thick, comprises many intercalations of pyrophyllitic schists associated with bed lenses of anthracite. The thickness of pyrophyllitic schist intercalations ranges from 0.2 to 10 m.

The Lower Liassic deposits of kaolin type (fireclays) pertaining to the Gresten facies, grade into pyrophyllitic schists; concomitantly, the weak metamorphosis of coals of the thick intercalations leads to formation of anthracite and transforms the finaly disseminated coaly matter into graphite. The main part of the central (produc-

tive) complex consists of chloritoid-quartzose pyrophillitic schists, deriving from the weak metamorphism of some sandy kaolins. The transformation of kaolinite into pyrophyllite, the grading of illite into sericite is noticed. Along fissures or in geodes there was encountered an almost pure pyrophyllite (only 4% nacrite), sometimes associated with quartz, pyrite or chlorite.

The pyrophyllitic schists are composed mainly of pyrophyllite (80—90%), followed by chloritoid (1—19%), sericite (1—10%) and kaolinite (nacrite (1—7%). There also occur quartz (1—4%), graphite (1—4%), iron oxides and hydroxides, sporadically diaspore, chlorite, carbonates, rutile, tourmaline, zircon, pyrite. In the Baia de Arieş area the pyrophyllitic schists include larger amounts of chlorite-kaolinite (about 40%) and more sericite than Schela-Viezuroui schists.

The pyrophyllitic schosts present a refractoriness of 158—169 PI and are utilized in refractories.

The Schela formation is intensively folded and dislocated by faults showing numerous boundinage and lensing phenomena.

SEDIMENTARY KAOLINS

Aghireş. In the north-western part of Transylvania there are important kaolin sandy deposits of Oligocene age developed, exploited in the Aghireş area (Corneşti quarry).

The productive bed is underlain and overlain also by kaolin-bearing levels which, however, do not present any economical value. The kaolin-bearing sand bed considered to be mined show a variable thickness, ranging from 2 to 8 m (in average 4 m).

The coarse fraction consists of quartz (80—85%), micas (up to 10%) and sporadically chlorite. Heavy minerals (tourmaline, hyperstene, diopside, ilmenite, magnetite, garnets, rutile, staurolite, hematite, apatite, pyrite) may be noticed. Goethite is a common mineral present as impregnation in sands.

The fraction below 63 microns represents 14—16% of the raw material. Mineralogically it is constituted of a well-crystallized kaolinite T (75—85%), hydromica (10—15%), quartz (5—10%) and iron oxides and hydroxides, carbonaceous matter and calcite.

The Aghireş washed kaolin is utilized in fine ceramics and refractories industry. The commercial product presents a refractoriness of 169—171 PI-.

Medgidia. The Aptian continental deposits of South Dobrogea include essential accumulations of weakly coherent kaolinitic clays well developed especially within Medgidia area.

The clay deposits occur as lenticular beds with variable thickness (0.2—20 m), and occasionally with great lateral extent (hundreds of meters). In the kaolin-bearing complex there are intercalated cross-bedded sands and gravels which may become dominant in some areas. The clays, sands and gravels are white, yellowish, grey, red, red-violaceous due to the Fe and Mn oxides and hydroxides. Blackish and grey clays may also occur within some horizons rich in carbonaceous matter. The Aptian deposits are overlying the Jurassic and Barremian limestones or even directly the greenschist basement, and are transgressively overlain by the Albian, Cenomanian, Turonian or Sarmatian deposits.

The mineralogical composition of the clay fraction is characterized by kaolinite, subsidiary illite and montmorillonite, with incidentally chlorite. Among non-clay minerals quartz, feldspars, calcite, siderite and goethite can be recognized.

The kaolinitic clay from Megdidia can be used in paper industry, in foundry and ceramic industry. The marketable product for refractories must have a minimal refractoriness of 165 PI, and for paper industry a minimal whiteness of 65%

RESIDUAL KAOLINS

Stejera. Kaolin-bearing rocks are represented by kaolinized gneisses and kaolinitic arkosic sandstones forming an irregular layer 0.8—6 m thickners. These deposits show a residual character representing an pre-Paleogene weathering crust of lateritic type, preserved under the Eocene transgressive deposits.

Kaolinitic sandstones consist of quartz and angular fragments of micaceous quartzite encompassed in a kaolin groundmass.

The fraction below 63 microns represents about 10% of the raw kaolin-bearing rocks and is composed of kaolinite, illite, haloysite, incidentally montmorillonite and chlorite; beside clay minerals quartz, feldspars, micas, goethite, dolomite, calcite, rutile and pyrite are encountered.

Sichevița. Another relic of fossil weathering crust is known at Sichevița. These residual deposits occur as an irregular layer of 0.2—9 m thickness represented by a quartzitic sandstone; at the contact level of sandstone and granite there are encountered lenses of white kaolinitic sands.

HYDROTHERMAL KAOLINS

Harghita. The rocks of the area consist of vocanogenic sedimentary formations, pyroclastics and lava flows which are overlying the crystalline basement and the Mesozoic and Tertiary sedimentary deposits. The effusive rocks encountered in this region are pyroxene andesites, pyroxene amphibole andesites, amphibole andesites, biotite amphibole andesites and basalt andesites.

Argillization, silification and pyritization are the main types of hydrothermal alteration and are often connected with volcanic craters.

Hydrothermally altered zones are nonhomogeneous, rendered impure by limonitization of pyrite and are also including partially argillized blocks.

In the advanced phase of argillization the following stages can be distinguished: a first stage of formation kaolinite, a subsequent one of formation of hydromica and a final stage of formation of montmorillonite, chlorite, vermiculite and mixed-layer minerals.

The commercial product called „colloidal kaolin" from Harghita is composed of 10.5 Å hydromica (over 90%), kaolinite (7%), swelling clay minerals and quartz (under 3%).

10.5 Å hydromica shows an advanced degree of dispersion, a very good orientation and a high crystallinity.

"Harghita kaolin" has low refractoriness, high plasticity and presents thixotropy. Its absorption capacity is 55—60% of that of washed kaolin. „Harghita kaolin' is used in the paper and fine ceramic industry.

Parva-Cormăița. In the Rodna Mountains the mesozonal crystalline basement is overlain by Eocene and Oligocene sedimentary deposits. These rocks are pierced by 3 rhyolite dykes at Parva and a subvolcanic biotite dacite body at Cormăița The eruptive rocks are more or less kaolinized.

In the Parva zone the rhyolites are hydrothermally altered by kaolinization, weak sericitization, pyritization and silification. The rocks are more strongly argillized where their fissuration is more intense.

Down to a depth of 40—50 m, weathering processes are superimposed on the hydrothermal alteration, leading to a more intense kaolinization, accompanied by montmorillonitization, calcitization and limonitization.

The mineralogical composition of the clay fraction is as follows: 55—76% kaolinite, 5—15% illite, 5—15% montmorillonite, 5—10% quartz, 0—5% feldspar and sporadically cristobalite and calcite.

The raw kaolin can be utilized in fine ceramics, due to its satisfactory contents of feldspar and quartz. The washed kaolinized rhyolite may be used in fine ceramic industry (pottery, electroporcelain), in paper industry, rubber, white cement, etc.

Concerning the kaolinized body of the Cormăiţa area, the following mineralogical composition of the clay fraction is to be noted: 35—50% kaolinite, 10—25% illite, 10—25% montmorillonite, 0—10% chlorite, 5—10% fedlspar, 5—7% cristobalite, 1% quartz.

The Cormăiţa kaolin can be utilized in ceramic industry.

OTHER HYDROTHERMALLY KAOLINIZED ZONES

At *Poienița-Brad* there are encountered kaolinized, silicified and pyritized andesites and tuffs with a reduced plasticity.

At *Cavnic-Roata* there is hydrothermal argillization of rhyolites and andesites. Argillization zones with kaolinite, illite, montmorillonite and weins formed of kaolinite, dickite and pyrophyllite occur.

At *Tarna* there are encountered zones of hydrothermal argillization of andesites and veins filled up with kaolinite and illite.

At *Groape-Tîrgu Lăpus* the crystalline formations are crossed by aplite and pegmatite veins which are intensely kaolinized in the neighbourhood of limestones under the action of hydrothermal solutions. Occasionally there occur kaolin pockets within limestones. The kaolinized material includes mostly well-crystallized kaolinite T (60—90%), montmorillonite (10—20%), illite (5—15%) and quartz (0—2%). The first argillization phase is the kaolinization, followed by montmorillonitization and chlorite-vermiculitization.

At *Măcin* the quartz porphyry and porphyrite veins are kaolinized owing to the circulation of hydrothermal solutions along the fault lines. The mineralcgical composition of the fraction below 10 microns is as follows: 60—80% kaolinite, 10—15% illite, quartz and felspar, 10—30% montmorillonite.

At *Valea Roşie* and *Valea Borcutului* there are outcrops of intensely kaolinized, pyritized and silicified andesites, dacites and rhyodacites. The washed kaolin consists of 50—70% kaolinite, 15—50% illite, 5—15% quartz and feldspar. The degree of whiteness ranges from 40 to 70% and plasticity ranges between 47—51.

At *Talagiu* the andesites underwent some hydrothermal alteration processes such as argillization, garnetization, propylitization, sericitization, chloritization, carbonation, opalization, alunitization, and pyritization. Argillization, the most widely spread process, is represented by montmorillonitization (40%), pyrophyllization (30%), kaolinization (20%) and illitization (10%). Refractoriness of pyrophyllite-bearing rocks is 163 PI and the degree of whiteness ranges from 71 to 79.

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KAOLINIZED ROCKS ON THE ISLAND OF LESBOS (GREECE)

G. KANARIS and P. MATTIAS

ABSTRACT

A description is given of the mineralogy and geology of the kaolin deposits of Lesbos (Greece) which are caused by the action of hydrothermal fluids on volcanic rocks, lavas and tuffs, having dacitic, rhyodacitic, latitic, andesitic, etc. chemism.

The major deposits are *Magaros-Arghenos, Aspres Petres, Stipsi* and *Mesotopos;* the first three are located in the northern part of the island, near the centre of Petra, the last one near the southern coast and the centre of Mesotopos.

Inside these deposits, through diffractometric and thermal (DTA and TG) methods and direct E. M. and S. E. M. observations, the following minerals were detected: kaolinite (type from pM to T), smectite (montmorillonite), a mixed-layer mineral of the I-MO type, open-layer illite, alunite, jarosite, cristobalite and marcasite, surely newly-formed, while quartz and feldspar are to be considered as "residual".

On the whole, the deposits of Aspres Petres and Mesotopos show a rather homogeneous mineralogy, where the always present kaolin minerals can be associated with sulphates, alunite and jarosite, or with silica phases, quartz and cristobalite; the remaining deposits, instead, feature a significant "zoning". The latter has kaolin in the central part while, at the periphery, essentially smectitic minerals can be noted, mostly associated with feldspar and sometimes illitic.

This diversity of alteration products is to be ascribed to the different degree of alterability and thus of acidity of the fluids altered. Indeed, the different rock permeability due to differentiated porosity and fracturing as well as temperature variations, allow the same fluids to undergo modifications, including the hypothesis of becoming enriched with ions derived from the same rocks subjected to alteration.

The chemism of the original rocks does not seem to have determined any substantial influence on the formation of the altered terms.

Finally, all the deposits formed "in situ" fall within the typical deposits resulted by the actions of hydrothermal fluids connected with a late volcanism. Additionally, they are arranged along the structural alignments typical of the island and of the adjoining region of Asia Minor (Turkey).

INTRODUCTION

It has been known for a long time that the island of Lesbos has first quality clays which resulted in mining processes of a certain interest. These special clays were used above all as refractory material and also, at times, for white cements with satisfactory results..

Although the industry used such materials and they were commonly referred to as "kaolin", there was no knowledge on their actual mineralogical composition.

This work purposes to cover this aspect by providing some essential data.

There are no recent deep studies on the island of Lesbos with the exception of those conducted by PRAGER [1966], which refer above all to the petrographic aspects of outcropping volcanites and by KANARIS [1976], who was the first to consider the kaolin deposits, supplying some data on their mineralogy, ore deposits and also on geological aspects. Except for von HAUER [1873] and FOUQUE' [1894], DE LAUNAY

[1897] was the first to provide detailed indications and petrographic descriptions on the island rocks. Other studies were made by PHILLIPSON [1910], with new interpretations to the geologic maps of the previous authors.

More recently, GEORGALAS [1949] studied some volcanites on the island, providing further chemical and petrographic indications. Furthermore, MARINOS [1953] described the deposit of Aspres Petres, considering the clays as refractory material.

Finally, geologic maps of the island are available on a scale of 1 : 50 000, published by the National Institute of Geologic and Mining Research of Greece (I. G. M. R.) in 1974.

GEOGRAPHIC ASPECTS

The island of Lesbos or of Mytilene belongs to Greece and more specifically to the group of islands of the northern part of the Aegean Sea. It is located 10 km from the Turkish coast and about 250 km north-east of Athens *(Fig. 1)*. It has a surface area of 1630 km² and it is the largest island among those of the northern Aegean Sea.

The island is like a right-angle triangle, where the longest side has a NW-SE direction. There are two important gulfs, Kalloni and Yera; the former allows the island to be divided in two areas, North-West and South-East, respectively.

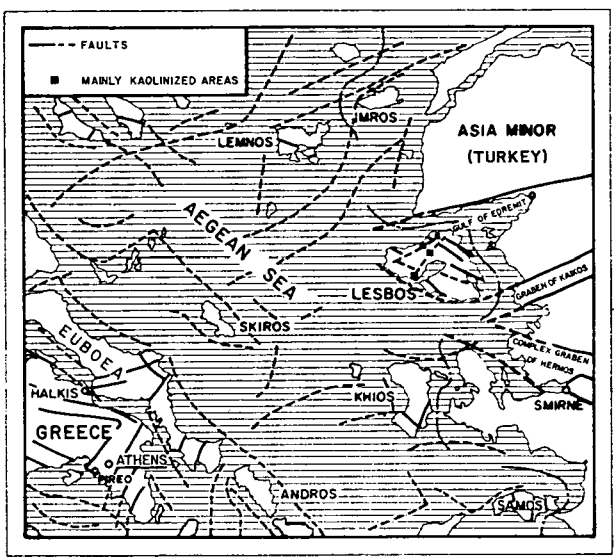

Fig. 1

GEOLOGICAL ASPECTS

The oldest outcropping rocks which form the island substratum are essentially made up by re-crystallized limestones of a white, gray and at times bluish color, of phyllitic rocks interbedded with arkoses and sandstones, sometimes with green schists, etc. The age attributed to this complex is from the Upper Carboniferous to the Permian *(Fig. 2)*.

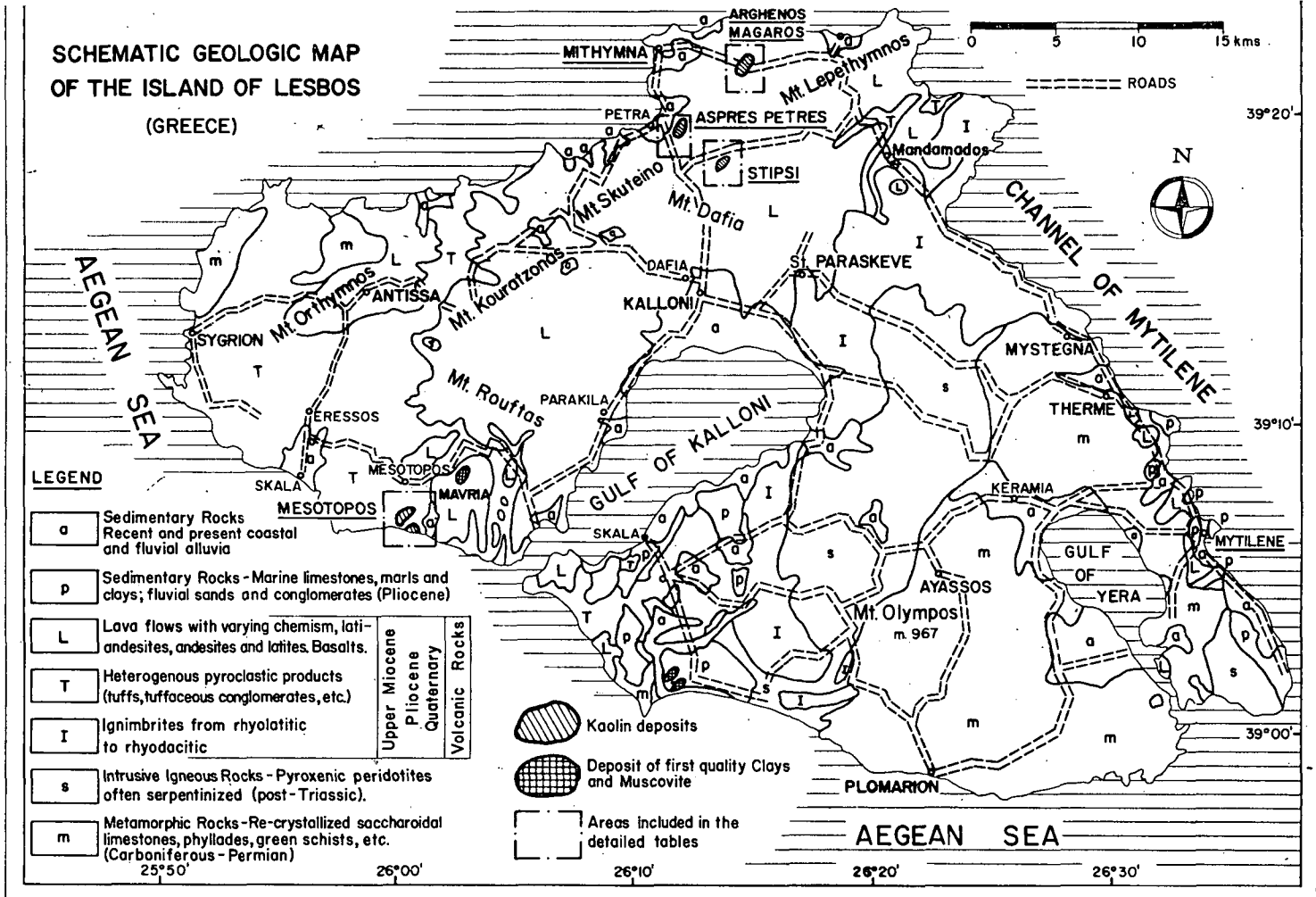
SCHEMATIC GEOLOGIC MAP
OF THE ISLAND OF LESBOS
(GREECE)
ARGHENOS
MAGAROS
MITHYMNA
Mt. Lepethymnos
0 5 10 15 kms
ROADS
PETRA
ASPRES PETRES
39°20'
Mandamados
STIPSI
N
Mt. Skuteino
Mt. Dafia
CHANNEL OF MYTILENE
DAFIA
St. PARASKEVE
AEGEAN SEA
Mt. Orthymnos
ANTISSA
Mt. Kouratzonos
KALLONI
SYGRION
MYSTEGNA
Mt. Rouftas
PARAKILA
ERESSOS
THERME
39°10'
GULF OF KALLONI
MESOTOPOS
SKALA
MAVRIA
KERAMIA
MESOTOPOS
SKALA
MYTILENE
GULF OF YERA
AYASSOS
Mt. Olympos
m. 967
LEGEND
a Sedimentary Rocks Recent and present coastal and fluvial alluvia
p Sedimentary Rocks - Marine limestones, marls and clays; fluvial sands and conglomerates (Pliocene)
L Lava flows with varying chemism, lati-andesites, andesites and latites. Basalts.
T Heterogenous pyroclastic products (tuffs, tuffaceous conglomerates, etc.)
I Ignimbrites from rhyolatitic to rhyodacitic
Upper Miocene
Pliocene
Quaternary
Volcanic Rocks
s Intrusive Igneous Rocks - Pyroxenic peridotites often serpentinized (post-Triassic).
m Metamorphic Rocks - Re-crystallized saccharoidal limestones, phyllades, green schists, etc. (Carboniferous - Permian)
Kaolin deposits
Deposit of first quality Clays and Muscovite
Areas included in the detailed tables
PLOMARION
AEGEAN SEA
25°50'
26°00'
26°10'
26°20'
26°30'

Fig. 2

The main outcrops are located near the eastern sector of the island; only two modest outcrops occur almost at the end of the western sector.

Then, a complex is found, with igneous intrusive rocks, defined as pyroxeni peridotites. Most of these rocks feature various degrees of serpentinizations an consequently a high degree of "alteration". The age of this intrusion is suppose to be essentially post-Triassic. This type of rocks outcrop with a rather elongate shape near the central-eastern sector. They are delimited eastwards by the Carboniferous-Permian complex and are covered westwards by successive volcanics fro the eastern sector of the gulf of Kalloni.

Since the Upper Miocene-Lower Pliocene, the previously described rock have evidenced an intense volcanic activity, heavily conditioned by epigenetic dislocations and faults, which has continued in the Quaternary; its products, more tha two-thirds of the island, have been ejected essentially in three periods.

In the first period, the volcanism was characterized by ignimbrites, locally followed also by heterogeneous pyroclastics. The main outcrops are situated near the central-southern borders NE of the gulf of Kalloni, and, with essentially tuffaceous products, in the western cape of the island.

In the second period, essentially latitic lavas were extruded, where latites, latiandesites, andesites and rhyodacites are, however, well represented. Such lavas constructed large volcanic structures which are aligned along significant structural trends, mainly E-NE and E-SE. In addition to small lava domes, large-sized lava flows ca also be found.

Within this activity, a "lower lava unit" and an "upper lava unit" were defined. The major outcrops of these products are located in the vicinity of the western an northern borders of the gulf of Kalloni and extend to the northern coast. Nonetheless, modest outcrops are present also in the southern sector.

The last period is characterized by silica-rich basalts, emitted above all by small scattered volcanic groups; they are represented by both lava flows and tuffaceous products.

From the Pliocene on, on an already essentially formed volcanic morphology, it is possible to observe locally rocks consisting of limestones, marls and clays of marine environment and sometimes clays, sands and conglomerates of continenta environment. Some of these products are occasionally interbedded in volcanic materials.

To complete the picture of the formations existing on the island, it is necessary to mention the products of the present waterway alluvia and of the coastal deposits, which have extremely varied lithologies.

TECTONICS

On the island of Lesbos, no great fault systems are evident. However, it is possible to deduce important structural alignments through volcanic occurrences, i. e. throug'i the trend of volcanic edifices, lava emission points and dykes. Based on th above, two main alignments can be defined. The first one is along E-NE and this i the alignment of the Lepethimnos, Skuteino, Kouratzonas and Orthymnos mountains and also of some dykes close to the centre of Dafia *(Fig. 1)*.

The second alignment is along E-SE and this is the main alignment of th Rouftas and Dafia mountains and of the Petra and Eressos dykes.

Nevertheless, these alignments are significantly parallel to the directions of the large epirogenetic faults which are observed in the Turkish territory, which the island of Lesbos can be considered as closely connected to, since it is likely to be a detached limb of such territory.

In particular, the faults of Edremit and of the graben of Kaicos follow the E-NE trend; while the complex graben of Hermos follows the second trend.

Considering the above, all the occurrences of alteration on the island of Lesbos, including the kaolin deposits discussed here, belong to the structural trend mentioned above.

THE KAOLIN DEPOSITS

On the island of Lesbos there are numerous kaolinizations, especially in the central-northern sector, however, the most important ones are Magaros-Arghenos, Aspres Petres, Stipsi and Mesotopos. Significantly, all of them are arranged along or slightly depart from the structural alignments mentioned above.

The first three of these deposits, Magaros-Arghenos, Aspres Petres and Stipsi, are located a few kms east of the centre of Petra, while the remaining one, Mesotopos, is near the southern coast, about 6 kms SE of Skala, Eressos and a few kms S of the centre of Mesotopos.

Finally, all four deposits are closely connected to volcanite alteration.

Magaros-Arghenos

The deposit of Magaros-Arghenos is the northernmost one and is located approx. 7 kms NE of the centre of Petra; it has a length of approx. 600 m and a width of approx. one hundred meters. Its elongation is E-NE (Fig. 3).

The kaolin derives from the alteration of latiandesitic to andesitic lavas belonging to the "lower lava unit"; it is whitish, always lithoid and massive and sometimes difficult to disagregate.

The mineralogic study conducted on the most significant samples evidenced the presence of the following minerals: kaolinite, quartz, alunite, feldspar, smectite (montmorillonite), mixed-layer minerals of the I-MO type, jarosite and doubtfully cristobalite and marcasite.

In addition to the specific composition of the most significant samples Table 1

TABLE 1

Magaros-Arghenos kaolin deposit (Island of Lesbos), semi-quantitative mineral composition (%).

(K=kaolinite; Sm=smectite, montmorillonite; A=alunite; J=jarosite; Qz=quartz; I-MO=mixed-layer mineral, illite-montmorillonite type; Fd=feldspar)

Sample	K	Sm	A	J	Qz	Others
16	55—60		10		30	Marcasite
18	70—75			5	10	I-MO (10—15)
845	65—70			5	25—30	
11	60		tr		30—35	
110		70—80				Fd (20—30)
17	10	45—50	5—10		10	Fd (25—30); cristobalite?

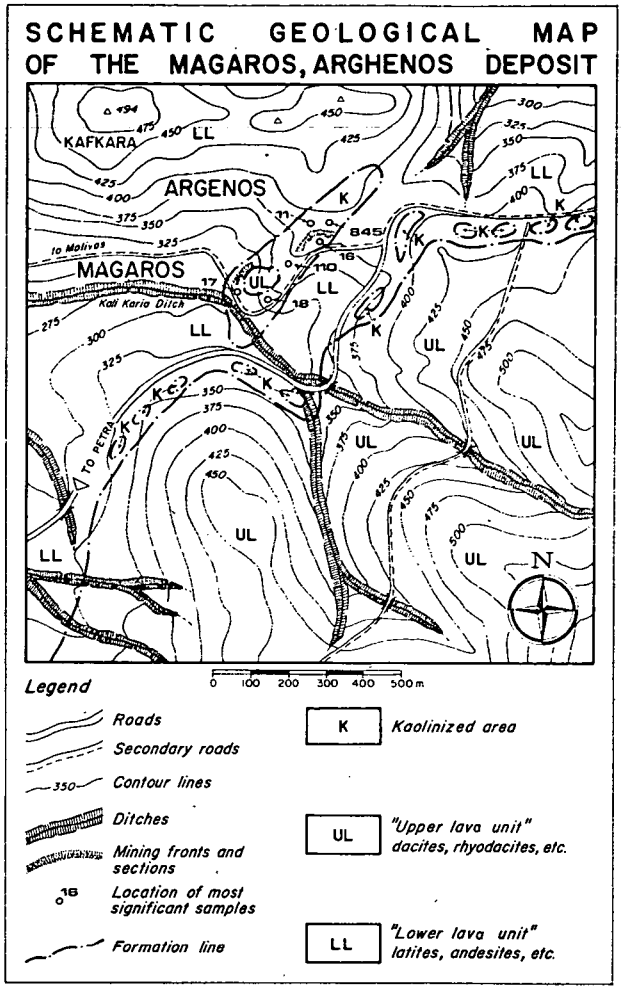

Fig. 3

also provides a semi-quantitative estimation of the various crystalline components obtained with diffractometric methods.[1]

Table 2 includes chemical analyses of the material studied from this area. Table 3, instead, exhibits some analyses of unaltered rocks from the literature related to volcanites from the alteration of which the kaolin deposits of the island are thought to be derived.

As it can be seen in Table 1, the mineralogical composition of kaolin is extremely varied. Kaolinite, usually of the pM type, is absent in some samples and reaches

[1] — The methodology of the works by GALAN HUERTOS *et al*; [1974]; POZZUOLI *et al.* [1972], SCHULTZ [1964], THOREZ [1976] was followed using particularly X-ray diffraction and thermal methods (DTA and TG), sometimes also direct electron microscopic (EM) and scanning electron microscopic methods.

TABLE 2

Chemical analyses of the kaolins from the Magaros-Arghenos, Aspres Petres, Stipsi and Mesotopos deposits of Island of Lesbos (Greece)

	MAGAROS-ARGHENOS			ASPRES PETRES					MESOTOPOS						STRIPSI Halatsia		STRIPSI Toubes		
	16	17	18	20	21	22	25	24	27	28	31	33	34	36	47	48	49	50	53
SiO_2	47,7	64,8	59,9	62,2	57,8	53,95	63,00	44,50	55,30	59,20	53,7	44,5	56,3	53,6	52,2	71,0	55,8	66.4	55.5
TiO_2	1.28	0,30	1.05	1.06	1.06	0.87	0.81	1.10	0.76	0.62	0.35	0.45	0.65	0.95	0.14	0.11	1.06	0.84	0.76
Al_2O_3	31.5	17.1	23.5	22.0	25.6	28.5	21.7	37.1	26.90	21.0	21.9	29.8	27.0	25.2	23.3	11.2	23.7	17.2	18.6
Fe_2O_3	1,96	1.35	0.86	0.49	0.73	0.68	0,28	0,65	0.55	0.93	0,91	2.99	0.32	0,73	0,45	0,44	1.63	1.15	4.20
CaO	0.24	0.54	0.39	0.30	0.42	0.31	0.54	0.13	0.29	0.26	0.19	0.26	0.29	0.29	0.17	0.17	0.16	0.14	0.28
MgO	0.10	0.46	0.22	0.07	0.12	0.07	0.05	0.09	0.18	0.15	0.09	0.20	0.23	0.34	0.06	0.08	1.04	0.98	1.76
MnO	0.04	0.06	0.01	0.01	0.02	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.03
Na_2O	0.03	1.38	0.04	0.04	0.05	0.07	0.05	0.04	0.07	0.08	0.05	0.10	0.18	0,50	0.08	0.10	0.05	0.07	1.14
K_2O	1.23	5.29	0.53	0.09	0.21	0.13	0.27	0.02	0.75	0.44	1,88	1.17	0.01	0.14	2.20	1.67	4.49	4.42	2.31
P_2O_5	1.44	0.71	2.11	1.69	2.20	2.06	2.27	1.03	1.88	1.72	1.72	1.99	1.03	1.81	1,72	1.42	1.21	1.49	0.89
Loss on ignition	12.50	5.40	10.35	10.38	10.70	12.30	9.03	13.90	14.20	12.10	17.22	16.90	12.70	14.70	17.70	11.00	7.60	5.44	11.55
SUM	98.02	97.37	98.96	98.33	98.91	98.95	98.01	98.62	98.81	98.61	98.02	98.37	98.72	98.27	98.03	97.20	96.76	98.15	97.02

16, 17, 18 = Kaolin from Magaros-Arghenos deposit.
20, 21, 22, 25 = Kaolin from main Aspres-Petres deposit.
24 = Kaolin from Aspres-Petres deposit, near Sizaksou.
27, 28, 31, 36, 36 = Kaolin from Mesotopos deposit.
47, 48 = Kaolin from Stipsi deposit, near Halatsia.
49, 50, 53 = Kaolin from Stipsi deposit, near Toubes.

TABLE 3

Chemical analyses of some unaltered volcanites of the Island of Lesbos (Greece)

	A	B	C	D	E
SiO_2	60.48	54.00	62.30	69.65	64.55
TiO_2	0.80	0.85	0.60	0.25	0.32
Al_2O_3	17.20	17.10	15.05	15.15	15.85
Fe_2O_3	4.25	2.86	4.10	1.35	1.85
FeO	0.85	3.60	0.70	0.55	0.85
MnO	0.15	0.28	0.10	0,05	0,08
MgO	2.58	4.90	3.20	0.35	1.40
CaO	4.30	5.20	4.65	0.90	2.05
Na_2O	3.96	3.76	3.40	3.90	3.70
K_2O	3.98	3.85	4.85	5.70	5.15
P_2O_5	0.31	0.58	0.45	0,08	0.14
H_2O^+	0.82	1.55	0.25	0.15	0.85
H_2O^-	0.04	0.02	0.75	1.10	3.20
CO_2	0.28	1.45			
SUM	100.00	100.0	100.40	99.18	99.99

A = "Andesinic doreite" by GEORGALAS [1949]
B = "Andesinic doreite" by GEORGALAS [1949]
C = "Phanero andesite" of Skala Sikamia by PRAGER [1966]
D = "Phanero andesite" east of Kliu by PRAGER (1966)
E – "Ignimbrite", Mt. Tavros by PRAGER (1966)

70—75% in other samples. Anyway, it is always associated with quartz and traces of alunite and jarosite.

Some samples have a dioctahedral smectite as single argillaceous component and then also mixed-layer minerals of the illite-montmorillonite (I-MO) type and feldspar as "residual" mineral of the original rocks. It is present in the samples containing the smectite component, whereas it is absent when kaolin minerals are predominant. The mixed-layer I-MO mineral is here associated with kaolin minerals, since feldspars are always absent.

Considering the sampling areas, the smectite-feldspar association can be supposed to be typical of a marginal or „boundary" area of the deposit of Magaros-Arghenos.

In the middle of the deposit, instead, kaolin minerals can be observe.

Additionally, in the mineralization area of Magaros-Arghenos, numerous small occurrences or evidences of kaolinization are found practically along the whole contact with the lavas of the "upper lava unit".

Aspres Petres

The deposit of Aspres Petres is located in the area SE of the centre of Petra (distance: 1.5 km).

The main part of the deposit extends for approx. 200 m, especially towards N-S, and has a length of some tens of metres *(Fig. 4)*.

Towards S-W, near Sizaksu, a modest alteration area is present, which is separated from the main part by about 300 m and closely connected to it genetically.

The rocks in the area are essentially dacitic, rhyodacitic, etc. lavas, belonging to the "upper lava unit".

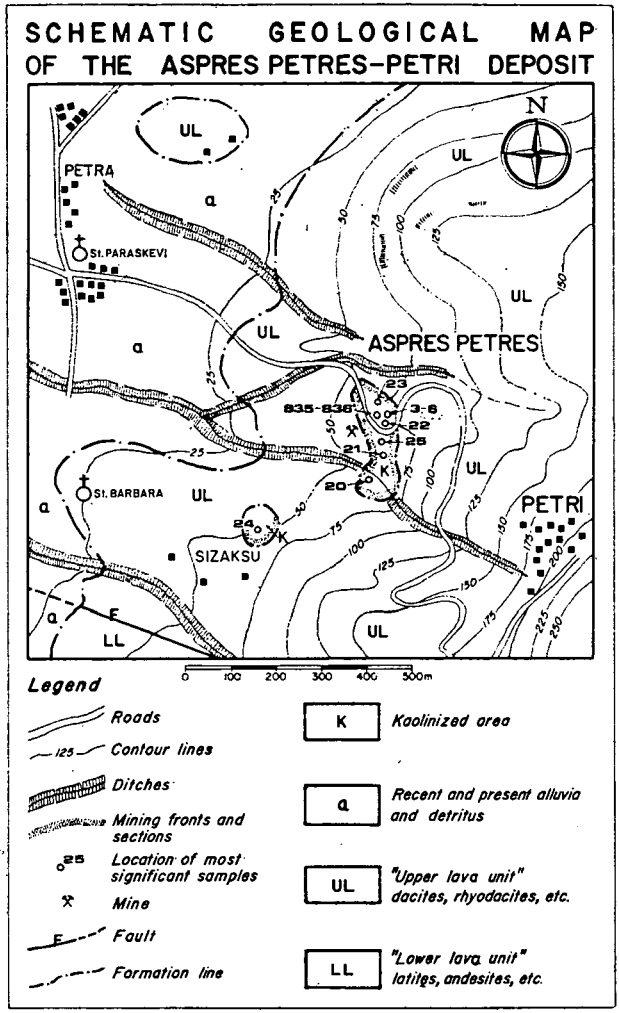

Fig. 4

Table 4 contains the mineralogical data concerning the most typical material of the deposit. The main association is kaolinite and quartz; traces or dobious evidences of alunite, jarosite, I-MO, marcasite and feldspar were detected.

Kaolinite, present in all samples examined together with quartz, proved to be the almost always predominant mineral. It has a rather varied crystallinity: in some samples it is poorly crystallized, in others it is well crystallized (T type).

Even sulphates, alunite and jarosite, although in traces, are almost constantly present.

Table 2 displays the chemical analyses of some samples studied which belong to this area.

On the whole, the material examined has a quite homcgeneos mineralcgical composition, since it is esentially constituted by kaolin minerals and quartz.

TABLE 4

Aspres Petres kaolin deposit (Island of Lesbos), semi-quantitative mineral composition (%)

(K = kaolinite; A = alunite; J = jarosite; Qz = quartz; Fd = feldspar; I-MO = mixed layer mineral, illite-montmorillonite type).

Sample	K	A	J	Qz	Others
20	70	tr	?	25	
21	80—85	tr	?	15	
22	85			10—15	Marcasite
23	90	tr		10	Fd (tr); I-MO (?)
25	70—75	tr	tr	25	I-MO (tr)
835	70			30	
836	70—75	?		25—30	
3	55—60	?		40—45	
6	40—45	?		50—55	
24	95		tr	tr	Marcasite; I-MO (?); Fd (tr)

Stipsi

The major kaolinization of Stipsi is located at Toubes, about 4.5 kms from the center of Petra, towards E-SE, and approx. 500 m S of the centre of Stipsi. It extends in the small valley between the top (level 330 m) and the centre of Stipsi for about 300—400 m *(Fig. 5)*.

The original rocks which determined the formation of the kaolin deposit mainly consist of latiandesitic, andesitic and latitic lavas, sometimes interbedded with lithic and even incoherent tuffaceous levels, all belonging to the "lower lava unit".

Another modest kaolinization is present in the vicinity of the southern side of the relief (level 455), at Halatsia, about 500 m E of the center of Stipsi.

In the latter case, it is essentially a level which has a thickness of some metres and which extends for about 200 m, comprised in highly silicified volcanites and is very close to a small fault with an approximate E-W trend, which crosses the Halatsia relief.

Also in this kaolin outcrop, the original rocks were of the same type as those belonging to the main outcrop.

Table 5 shows mineralogical data concerning the most typical litholcgic aspects of the two outcrops. Kaolinite, quartz, alunite, jarosite, illite, mixed-layer minerals of the I-MO type, smectite (montmorillonite) as well as cristobalite of significantly varied thermal state were identified.

It can be noted in Table 5 that the mineralogical composition is very varied for the Toubes area and relatively also for the Halatsia area. In some samples from Toubes, the kaolinite component may be absent, while in the samples from Halatsia it is always present with values form 30 to 60%. Always present in all the samples, instead, are sulphates, alunite and jarosite and silica phases, quartz and cristobalite. Smectite seems to appear near the outside borders of the alteration area of Toubes and thus similarly to what was observed for the kaolin deposit of Magaros-Arghenos *(Fig. 6)*.

At Toubes, illite proved to be one of the main components, however, always without feldspar and with traces of I-MO and smectite.

This considerable variability in mineralcgical composition is also confirmed by

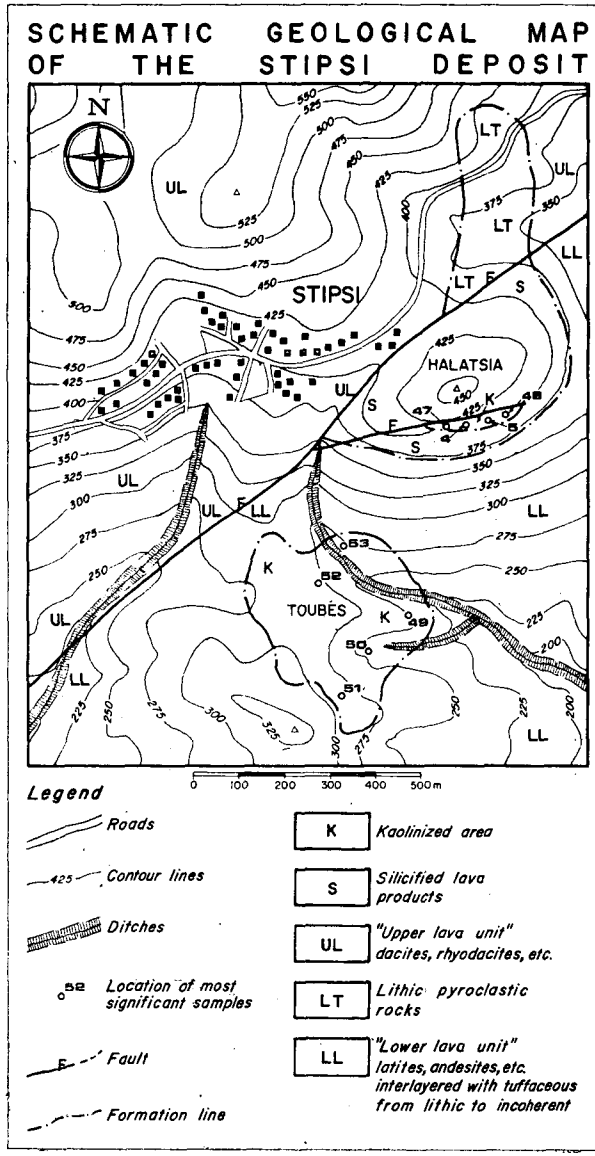

Fig. 5

the chemical analyses shown in Table 2, where the main oxides, silica, alumina, iron and potassium show extremely varied values for loss on ignition.

This variability is probably due to the considerable litholcgic variaticn of the volcanites outcropping there; these, besides a different chemism, show an extremely variable porosity due to essentially tuffaceous and massive lava elements.

It is necessary to underline that the small Halatsia outcrop is located in a very extensive area which was subjected to an intense silicification.

TABLE 5

Stipsi kaolin deposit (Island of Lesbos), semi-quantitative mineral composition (%)

(K = kaolinite; A = alunite; J = jarosite; Qz = quartz; I-MO = mixed-layer illite-montmorillonite type; Cr = cristobalite; Fd = feldspar)

Sample	K	A	J	Cr	Others
47	30—35	30—35		30	
48	40				Cr (55—60);
4	55—60	?			Cr (40—45)
5	45—50	5		50	
49	15		10	10	Smectite (tr); I-MO (tr) Illite (60—65)
50	10		tr	20—25	Illite (60—70)
53			40—45	10—15	Smectite (30—35); Fd (10); Cr (tr)

Both the alteration areas, Toubes and Halatsia, can be considered as arranged on the southern side of the SW-NE-trending fault, which delimite the complex of the "lower lava unit" from that of the "upper lava unit".

Mesotopos

It is the kaolin deposit located in the vicinity of the southern coast on the western side of the island of Lesbos.

On the sides of the Malas Mountain (165 m), approx. 2 kms S of the centre of Mesotopos and approx. 6 kms SE of the centre of Skala, Eressos, numerous kaolinization occurrences can be found, some of which enabled the development of mining processes, particularly at Korakes, near the southern coast. However, the most extensive areas are near the western side of the Malas Mountain, approximately along a N-NE and S-SW alignment *(Fig. 7)*.

The most significant samples, collected in the proximity of all outcrops reported, showed a quite homogeneous mineralogy. Indeed, kaolin minerals were determined in all samples but with a percentage varying from 40—45 up to 90%, in areas where the latter minerals are also the most frequent; only one sample exhibitde a lower amount of kaolin minerals (25%) (Table 6).

TABLE 6

Mesotopos kaolin deposit (Island of Lesbos), semi-quantitative mineral composition (%)

(K = kaolinite; A = alunite; J = jarosite; Cr = cristobalite; Qz = quartz; Fd = feldspar)

Sample	K	A	J	Cr	Others
27	65—70	15	tr	15	Marcasite (tr)
28	90	10			
29	95	?			
30	25	70		?	
31	40—45	20—25		30—35	
32	95		tr	?	Fd (tr)
33	95		tr		
34	95			tr	Qz (tr); illite (tr)
35	60	tr	tr	35	Qz (tr); marcasite (tr)
36	95		tr		Qz (tr); marcasite (tr)

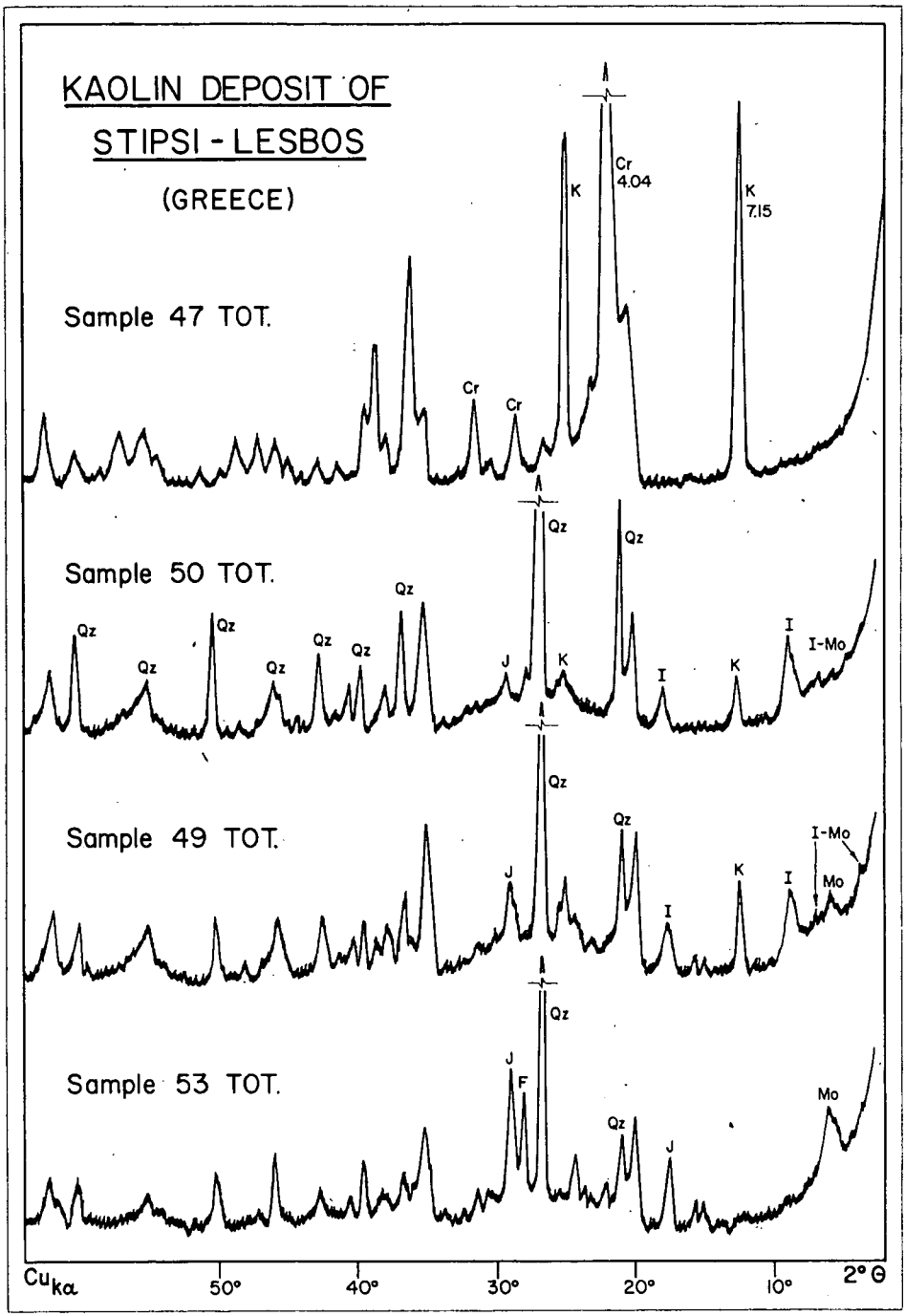
KAOLIN DEPOSIT OF
STIPSI - LESBOS
(GREECE)
Sample 47 TOT.
Sample 50 TOT.
Sample 49 TOT.
Sample 53 TOT.
K
Cr
4.04
K
7.15
Cr
Cr
Qz
Qz
Qz
Qz
Qz
Qz
Qz
Qz
J
K
I
K
I
I-Mo
Qz
Qz
J
K
I
K
I
I-Mo
Mo
Qz
J
F
Qz
Qz
J
Mo
Cu kα
50°
40°
30°
20°
10°
2° θ

Fig. 6

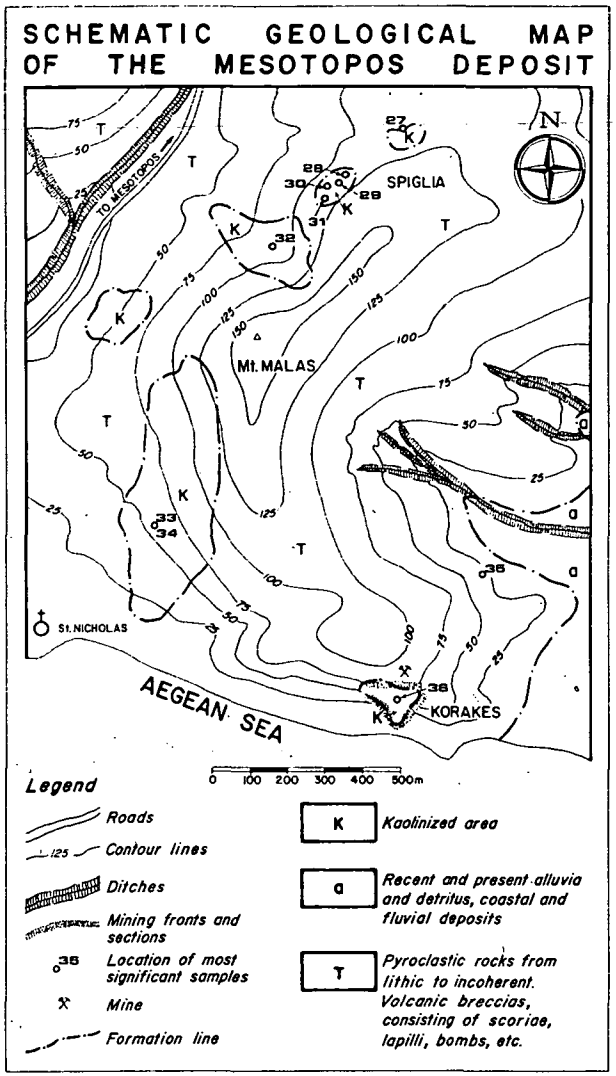

Fig. 7

Sulphates, alunite and jarosite, are constant, though in extremely variable amounts, from traces to 70%.

Crystallized silica, when present, appears almost exclusively as cristobalite. It is to be noted that this mineral occurs with a rather varied thermal state both in the deposit and in the sample examined, thus indicating the changing environmental and microenvironmental conditions. Among other minerals, mention should be made of marcasite, illite and feldspar either as dubious evidences or in traces. Kaolinite in this area is usually not well-crystallized (pM type) and sometimes the presence of halloysite was also supposed.

Table 2 indicates some chemical analyses of typical materials belonging to this area. There is a rather homogeneous chemical composition, which confirms what was observed mineralogically.

The rocks surrounding the kaolin outcrops, unaltered, consist of essentially pyroclastic products where typically cineritic levels are interbedded with lapilli levels containing blocks, volcanic bombs etc.

The relative homogeneity of the mineralogical composition, also confirmed by chemical analyses, suggests that the original volcanites have had quite constant physico-chemical characteristics and the alteration fluids must have acted on them under almost uniform conditions Moreover, there are evidences that the alteration area is much wider and that it also involves the eastern side of the Malas mountain, where significant small evidences of alteration locally appear.

DISCUSSION AND CONCLUSIONS

This study allowed to confirm that all the materials reviewed should be considered as "kaolins", except for only some of them coming from the deposits of Magaros-Arghenos and Stipsi, where the kaolin minerals can even be completely absent.

Furthermore, considering the geological-structural aspects, it can be supposed that all the kaolin deposits of Lesbos genetically belong to those of hydrothermal origin which formed "in situ" at the expense of volcanic rocks and which have a quite acid chemism. Considering the recent classification [KUŽVART, 1977], these deposits can hardly belong to those of "hydrothermal-solfatara" type. Additionally, the action of hydrothermal fluids must have occurred essentially in the final phase of the volcanic emissions on the island.

The newly formed material, i. e. kaolin, is generally massive, lithoid and difficult to disaggregate; if plunged in water it does not lose its cohesion; usually, it is whitish but sometimes it may be white-violet and white-pink.

The kaolin proved to consist of kaolinite and, almost constantly, of sulphates, alunite and jarosite, either in traces or as main mineralogical components.

Instead, when kaolin minerals are scarce or absent, there is a predominance of smectites, illites, or of silica, quartz and cristobalite minerals, in addition to sulphates.

The major possible mineralogical variations were found in the deposits of Magaros-Arghenos and Stipsi, while in the other deposits limited homogeneity was observed.

Nonetheless, even in the areas where kaolinite prevails, crystallinity is very variably; from poorly-crystallized types (pM), all transitions to well organized types (T) can be noted. This confirms that environmental and microenvironmental conditions must have been non-homogeneous, even in the kaolin alteration areas.

It is necessary to add that the cristobalite observed, with its different thermal states, suggests also the variability of environmental and microenvironmental conditions.

By comparing Tables 2 and 3, containing the chemical analyses of kaolinized and unaltered rocks, it is possible to note a general specific decrease in K, Na, Mg, Ca ions with more modest Fe values.

Silica may be very high in some cases and more reduced in others. Alumina always shows an increase and sometimes it has almost doubled values.

By examining the analyses of the mineralizations from the same deposit, the most considerable variations in compositions occur near the deposits of Magaros-

Arghenos and Stipsi, especially for silica and alumina values and partially for loss on ignition.

The K in the deposit of Magaros-Arghenos ranges from 0.5 to 5.29%, and Na from 0,03 to 1.38.

In analyses referring to the deposits of Mesotopos and Aspres Petres, instead, there is a lower variability in chemical composition. Without entering into details, all this agrees with what was observed on the mineralcgical composition of kaolin materials.

This compositional variability may be justified by the litholcgic diversity of the original rocks, especially as concerns their fracturing and porosity rather than their chemism. Indeed, while the chemism of the original rocks in all the deposits should be considered as rather homogeneous and acid when dacites, rhyodacites and andesites are present, there are, instead, considerable variations in appearence, permeability etc. of the rocks.

In particular, in the deposit of Magaros-Arghenos, a wide "zoning" was observed; from a core essentially made up of kaolin, i. e. where kaolinites are prevalent, there is a gradual transition towards areas where micaceous, illitic and smectitic minerals predominate. Smectite is associated with feldspar, which is entirely absent, instead, in the central alteration area. This observation allows to consider that alteration was more intense in the core, whereas, in marginal zones, the fluids acted progressively in a less aggressive way, so that it was possible to find feldspar.

Then, taking into account the mineralogical associations identified, especially in the zoned deposits, the development of the alteration process can be reconstructed.

First of all, it is possible to consider the condition when the abundant and acid fluids attack feldspathic volcanites having physically and chemicallyl homcgeneous characteristics, including fracturing, porosity and thus permeabiltiy. In this case, the alteration process gives rise to kaolinite minerals and possibly, at the local level, to silica-rich minerals, especially in areas where the actions were more intense.

If the fluids, always originally acid, are not particularly abundant and have difficulties in permeating feldspathic rocks, they can directly produce kaolinite minerals close to their emission area. Towards the outside, instead, their influence and aggressivity become gradually modified, leading to the neoformation, for these areas, of essentially micaceous minerals (illite). Even if the fluids are less aggressive, their energy is sufficient, als in this case, to bring about a complete alteration and transformation of feldspars.

Then, towards the outside, there is an area where feldspars are present, thus showing a decreased altering capacity of the fluids. The newly formed components of this area are smectitic, therefore belonging to a pH environment more basic than that in the preceding areas. It should be underlined that sometimes mixed-layer minerals of the I-MO type were found, which can be interpreted as newly formed minerals marking the transition between illite and smectite areas. Due to the progressive variation in the environment, these minerals may form, considering the strong structural analogy between the two minerals, with the progressive modification of the interlayer space. In conclusion, these minerals express conditions of transitional environments, where illite is not entirely stable and, at the same time, where smectite does not reach its typical conditions completely.

Mixed-layer minerals, instead, cannot be present between illite and kaolinite areas, where the structural patterns of the two minerals show too marked differences. But it should be emphasized that the literature reports occasional finds of a mixed-layer mineral of the kaolinite-smectite type, however in particular genetic environ-

ments, where the alteration conditions discussed here do not occur SCHULTZ, L. G. *et al.*, 1971; WIEWIORA, A., 1971; WILSON, M. J. *et al.*, 1972].

The alteration evolution might be characterized by the following sequence of newly-formed mineral areas:

— kaolinite areas (with different crystallinity)
— illite areas
— area with mixed-layer I-MO minerals
— smectite area (montmorillonite, possibly with feldspar).

The relative zoning was directly checked on site in the deposits of Magaros-Arghenos and at Toubes, deposit of Stipsi.

The existence of possible "zonings" in the kaolin deposits has been known for a long time. They were described in deposits from alteration of both instrusive igneous rocks [SALES *et al.*, 1948; KERR *et al.*, 1950] and volcanic rocks [LOVERING, 1949].

MINATO recently [1976] reported these characteristics for the kaolin deposit of Itaya (Japan), where the kaolin „mine" is surrounded by a belt of smectitic materials, all generated by the same hydrothermal events.

It should thus be admitted that the fluids with marked acid and, therefore, agressive characteristics may have become enriched in ions deriving from the same rocks during their flow from the central area and their lateral permeation, in connection with the local permeability. This fact led to a variation of the chemism of the same fluid towards more basic elements, with a consequent variation of its aggressivity, showed by the "residual" feldspar. Temperature values, too, may have decreased accordingly.

As concerns the kaolin deposits of Aspres Petres and Mesotopos, zonings affecting the whole outcrop were not noted, perhaps because the physical characteristics of the rocks are rather homogeneous, especially their permeability.

A characteristic more or less common to all mineralizations is a possible compositional variability of altered rocks, without excluding, however, the existence of "cores" with a homogeneous composition.

If the trend of the outcrops in the mineralized areas is examined, a preferential orientation can be generally noted, which agrees with the large regional tectonic trends of the Asia Minor territory. And the island of Lesbos is obviously affected by these trends.

In particular, in all the deposits, the NE trend should be regarded as preferential in the development of the mineralization process and thus belonging to the large tectonic trends.

The mineralization of Aspres Petres, too, is characterized by the above direction when the main alteration area is connected with the area of Sizaksu.

These structural geological considerations were drawn based only on surface survey data. In the light of all the observations, it can be stated that the deposit of Mesotopos is the most important, followed by Aspres Petres, Magaros-Arghenos and Stipsi.

To complete these considerations, it should be mentioned that on the island there are other alteration areas, the most important of which is Mavria.

In these areas, which can always be connected to the regional tectonics, smectitic minerals seem to prevail; in this instance, the alteration process should be considered in the light of the above, as a rather "initial" phase or better a phase where the ifluds are more markedly basic.

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DIAGNOSTIC TESTS FOR EVALUATION OF KAOLIN PHYSICAL PROPERTIES

HAYDN H. MURRAY

ABSTRACT

Kaolin is an important industrial mineral which is used by many process industries including paper, paint, plastics, ceramics, rubber, and many others. Several standard tests must be performed to fully evaluate the economic potential of kaolin. These include mineralogical determinations by X-ray diffraction, scanning electron microscopy, differential thermal analysis, and the petrographic microscope; particle size distribution; grit percentage (material larger than 44 microns); color (brightness and whiteness); viscosity; resistivity; particle shape; beneficiation response (chemical leaching, flotation, high intensity magnetic separation); ceramic tests (green, dry, and fired strength, shrinkage, fired color, porosity, fusion temperature); and surface area. Other tests that are used include oil absorption, gloss, opacity, abrasion, moisture, pH, reagent demand, and others.

INTRODUCTION

Kaolin is one of the most versatile of the industrial minerals [MURRAY, 1977] in that it is so extensively used for so many applications [MURRAY, 1963]. Many new uses are being discovered for this versatile mineral each year. It is a unique industrial mineral because, except for catalytic activity in some organic systems, it is chemically inert over a relatively wide range of pH values; is white or near white in color; has good covering or hidding power when used as a pigment of extender in coating and filling applications; is soft and non-abrasive; has low conductivity values of both heat and electricity; and is lower in cost than most materials with which it competes. Some uses of kaolin require very rigid specifications including particle size, brightness, color, and viscosity. On the other hand some uses have no critical specifications, i. e. cement, where the only concern is light color and chemical composition. Ceramic specifications are variable in that each user may have slightly different requirement as to strength, pyrometric cone equivalent (PCE), plasticity, and color depending upon the body formulation. In general the value of a kaolin product is based upon color, brightness, and particle size with a white, bright, fine particle size kaolin having the highest value.

This paper will outline and discuss some of the basic tests for evaluating a kaolin deposit particularly for use in paper, paint, ceramics, rubber, plastics, and some other applications. The matter of drilling, sampling, and calculating reserves, which are very important, will not be discussed in this paper.

The following definition of kaolin is used in this paper: "kaolin is a clay consisting of substantially pure kaolinite, or related clay minerals, that is naturally or can be beneficiated to be white or nearly white; will fire white or nearly white; and is amenable to beneficiation by known methods to make it suitable for use in whiteware, paper, rubber, paint, and similar uses. The term is applied without direct

relation to the purity of deposits. Many kaolins are sedimentary or secondary in origin and are very pure and required very little concentration of beneficiation in preparation for market. Many other kaolins are primary (hydrothermal or residual) in origin and contain as little as 10 percent kaolinite which requires considerable concentration and beneficiation to recover a marketable kaolin.

The largest single user of kaolin is the paper industry which accounts for almost 70 percent of the shipped tons in the United States and about 50 percent of the world tonnage. It is estimated that the world tonnage is approximately 17 million with 7 million being produced in the United States and 3.5 million in England. Thus it is evident that over half of the world's tonnage comes from two areas; Southeastern United States, i. e. Georgia and South Carolina, and Southwestern England — the Cornwall area.

Evaluation tests to determine the physical properties of kaolin are very important because different kaolin deposits can give such different test results. If one took a very fine particle size kaolin and a very coarse particle size kaolin and compared many of the physical properties the results would make one conclude that they were testing different minerals. There are many tests that are used to evaluate kaolin but only the more important will be discussed in this paper. The tests will be divided into sections, general evaluation, paper, ceramics, rubber, paint, and other uses.

GENERAL EVALUATION TESTS

In order to fully evaluate potential uses of kaolin many tests are necessary; however, a series of tests that will give a good indication of some of the more important physical properties and can be used as screening tests especially for coating, filling, and extender applications are as follows:

1. Mineralogy
2. Screen Residue (GRIT)
3. Particle size distribution
4. Brightness
5. Viscosity
6. pH

Mineralogy — The mineral content of a kaolin is very important in assessing the applications and the results of many tests for determining the physical properties and also for determining the beneficiation processes that may be needed to produce a saleable product. X-ray diffraction of the whole sample will give a quick assessment of the gross mineralogy but in many instances minor quantities of illite and smectite will not be detected. Separation of the 2 micron fraction and the 0.5 micron fraction and making oriented slides will enhance the basal reflections of the clay minerals and enables one to detect the presence of very small quantities of these layer silicates. The presence of quartz, cristobalite, alunite, smectite, illite, muscovite, biotite, chlorite, gibbsite, feldspar, anatase, pyrite, or halloysite certainly will effect the beneficiation steps and the possible uses of the kaolin. In many instances one cannot detect the presence of halloysite in the kaolin using X-ray diffraction techniques and so it is prudent to make some scanning electron micrographs and/or a differential thermal — thermal gravimetric analysis to detect either hydrated halloysite, alunite, gibbsite, or smectite. The presence of smectite and/or alunite in the kaolin causes high viscosities, halloysite also causes high viscosity and lowers the opacity of hiding power, and quartz and/or cristobalite in the finer particle sizes gives high abrasion values. X-ray diffraction can also be used to determine variations in kaolinite crys-

tallinity which has a marked effect on physical properties [MURRAY and LYONS, 1956].

Screen Residue (Grit) — This test gives the percentage of particles that are retained on a 325 mesh screen (44 micron openings). Quartz, mica, and feldspar along with agglomerates of tightly bonded clay are the most common minerals retained on the screen. The percentage of the screen residue is important in determining the percent recovery of minus 44 micron material as it is this fraction that is the more important in either wet or dry processing plants. The procedure is described as method T681-SU-71, a standard procedure published by the Technical Association of the Pulp and Paper industry. The procedure involves weighing out a specified amount of kaolin, dispersing the kaolin in a measured amount of water, blunging the clay on a high speed mixer for a specified time, screening, drying, weighing, and determining the percentage of material retained on 325 mesh screen.

Particle Size Distribution — Particle size distribution is one of the more important properties of the kaolin as it effects viscosity, brightness, opacity, gloss, ceramic strengths and shrinkage, and many other properties. Sedimentation methods based upon Stoke's law are utilized for measuring particle size. The results are expressed in terms of "equivalent spherical diameter" (esd), the diameter of a sphere having the same specific gravity that settles at the same rate as the particle in question. Kaolin particles are platy or blocky, not spherical, but the results of a sedimentation analysis can be correlated with some physical properties relating to coating kaolins, filler and extender kaolins, and ceramic kaolins. Procedures limited to gravitational sedimentation are inaccurate for kaolin particles finer than 1 micron in e. s. d., and centrifugal procedures are used to determine the sizes below 1 micron e. s. d. Standard method T649-SU-68 of the Technical Association of the Pulp and Paper industry is the suggested method for determining the particle size distribution of kaolin. This TAPPI method outlines the procedure to follow, the apparatus needed, how to calculate e. s. d., and how to report the results.

Brightness — the brightness of kaolin is a most important physical property because it determines the potential uses and prices that can be charged. In general the higher the brightness of the kaolin the more valuable it is. Again the Technical Association of the Pulp and Paper industry has published a standard method T646-73 for measuring brightness. The standard brightness values are measured at 457 millimicrons and the standard (100%) against which the samples are compared is smoked magnesium oxide. The TAPPI method outlines the way in which the sample is to be prepared in order to achieve reproducible results and gives the type of instrumentation that is used to make the measurement at 457 millimicrons.

Viscosity — Flow properties of kaolin slurries are very important determinations because kaolin is used in slurry form in so many industrial application and particularly in two of the largest user industries, paper and paint. Again the Technical Association of the Pulp and Paper industry has published TAPPI method T648-SU-72 which describes the apparatus, calibration, who to report the results, and the precision of the test. Measurements of viscosity of the kaolin — water slurries are made at precise solids levels which is 70 percent for the sedimentaray kaolins of Georgia. Low viscosity clays are requried in the paper industry because the kaolin coating color must flow easily as it is applied to the paper sheet and not leave streaks and blotches which can be caused by high viscosity coating colors.

pH — The pH of untreated kaolin slurries normally ranges from 4.5 to 6.5. A high pH generally indicates the presence of soluble salts which if they are not

removed, can cause severe problems in many applications. The technical Association of the Pulp and Paper industry has published TAPPI method T667-SU-75 which describes the determination of the hydrogen-ion concentrates (pH).

EVALUATION TESTS FOR USE IN PAPER

The paper industry is by far the largest user of kaolin. Kaolin is used both as a filler in the sheet and as a coating ingredient on the surface of the sheet Many special tests have been designed to evaluate kaolin as a filler clay in paper and as a coating clay on the paper. Some of the more important tests are listed as follows and will be described briefly.

1. Percent recovery as coating clays
2. Rheology of medium and fine particle size fractions
3. Color improvement (chemical, flotation, magnetic)
4. Dispersability and Disintegration
5. Sheet properties
   a) brightness
   b) whiteness
   c) opacity
   d) gloss
   e) smoothness
   f) ink receptivity
   g) film strength
6. Adhesive demand

Percent recovery as coating clays — The most important size fraction of kaolins for producing a coating clay is that portion 2 microns and less. The major coating clay used for publication grade paper contains 80 percent of the particles finer than 2 microns and for cover stock, calendars, company reports, etc. requires a coating clay with 92 percent or more of the particles below 2 microns. Therefore it is necessary to make fractionations in the laboratory and calculate the percentage of particles less than 44 microns, less than 2 microns, and less than 0.5 microns. Screening and gravity settling is generally used to make the separations and the results are calculated as percent finer than 2 microns.

Rheology — Fluid dispersions are prepared at a given percent solids and low shear and high shear viscosity are measured. Low shear rheology seems to be controlled primarily by surface area, with viscosity increasing with decreasing particle size. High-shear rheology seems to be controlled largely by particle packing. *Fig. 1* shows the relationship between particle packing and viscosity. The dashed lines represent the effective volume of each particle. The right hand side of the diagram shows that high solids clay suspensions can be obtained most efficiently with random size distributions. *Fig. 2* shows the three types of viscous flow that are of particular interest in paper coating kaolins. Newtonian flow occurs when the viscosity remains constant as the shear rate is increased or decreased; thixotropy occurs when the viscosity decreases as the rate of shear is increased; and dilatancy occurs when the viscosity increases rapidly as the rate of shear increases. Measurements of viscosity of the clay-water slurries are made at precise solids levels, usually 70 percent for Georgia coating clays. Low shear viscosity is usually 30 centipoise or less at 20 revolutions per minute using a standard Brookfield viscosimeter, the standard unit used to meas-

ure low shear viscosity. High shear viscosity is measured using a Hercules viscometer [MURRAY, 1976].

Color improvement — Most kaolins require color beneficiation to get the maximum brightness and whiteness from the product. The most common method used to improve color is to chemically leach the soluble iron from the kaolin. The kaolin slurry is acidified, using sulfuric acid, to pH 3 and then a strong reducing agent sodium hydrosulfite is added (0.3 to 0.5 percent by weight equivalent of SO_2 on the weight

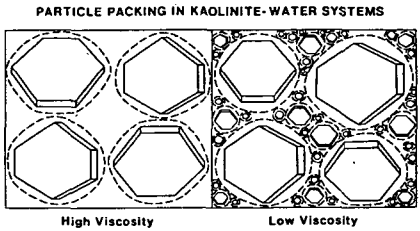

Fig. 1. Relationship between particle packing and viscosity

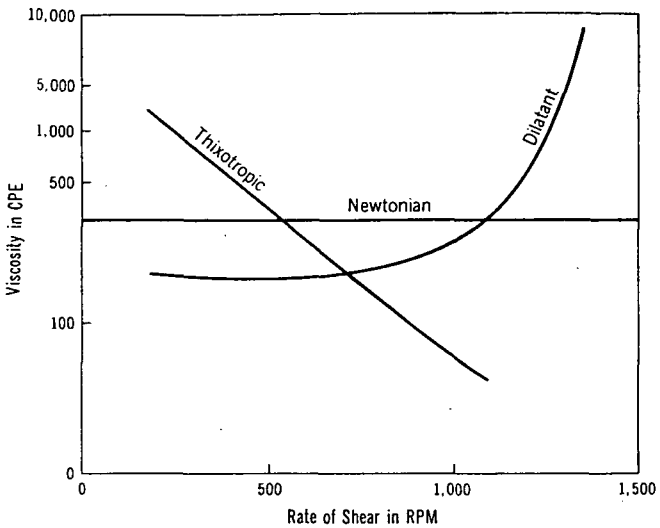

Fig. 2. Types of viscous flow

of dry clay) to reduce the iron to produce a soluble iron sulfate which is removed in the filtrate as the clay is dewatered by filtration. This leaching of soluble iron can significantly improve the color in many kaolins. High intensity magnetic separation will remove the iron and titanium minerals *(Fig. 3)* and produce a significant improvement in color [IANNICELLI, 1976]. Flotation also removes iron and titanium minerals and the resulting product is very white and bright [GREENE and DUKE, 1962].

Dispersability and disintegration — In order to achieve optimum results with a coating clay the kaolin particles must be completely dispersed. Many kaolins are easily dispersed using small amounts (0.2 to 0.5 percent) of alkali phosphates and silicates. In order to be utilized as a paper coating clay the kaolin must be able to be

easily dispersed. Disintegration is a measure of the presence and amount of clay agglomerates in a coating clay. Aggregations of clay particles are caused during processing because of cementation or sintering and are difficult to disintegrate during normal makedown of the coating clay. The disintegration test consists of the application of a controlled amount of work which is sufficient to disperse the normal kaolin slurry. After this work is applied to the kaolin slurry, the slip is poured through a 325 mesh sieve and the agglomerates remain on the sieve and the amount can be determined.

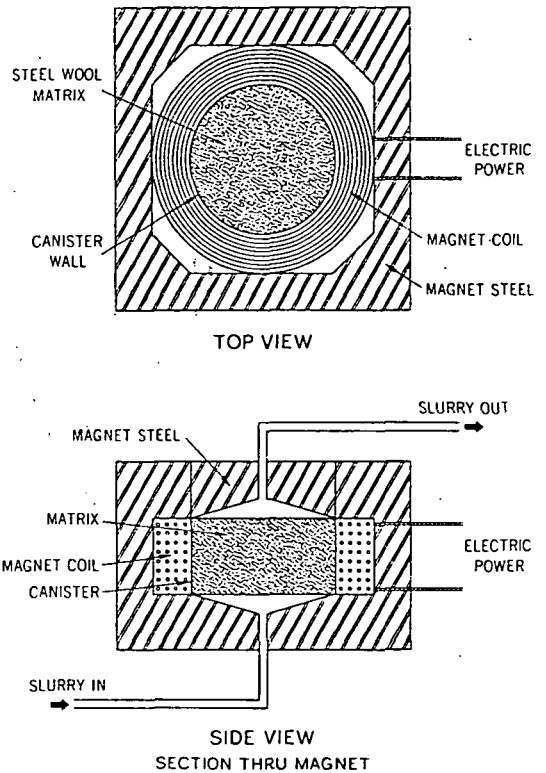

Fig. 3. Diagrammatic representation of high intensity magnetic separator

Sheet properties — Standard sheets of paper can be coated with a coating color consisting of kaolin and binder using standard procedures as outlined by the Technical Association of the Pulp and Paper industry. The coated sheet must be conditioned, calendared, dried and have a known amount of coating on the surface. Many properties can be measured and compared such as brightness, whiteness, opacity, gloss, smoothness, ink receptivity, and film strength. All these test procedures are available as TAPPI standards from the Technical Association of the Pulp and Paper industry [BRITT, 1970, p. 665]. These tests enable one to evaluate the properties of a particular clay for use for coating paper.

Adhesive demand — This is another standard test of the Technical Association of the Pulp and Paper industry. An adhesive such as starch or latex binds the kaolin

particles together and to the sheet of paper. The adhesive is much more expensive than the clay so the minimum quantity that will give the necessary binding is used. A high surface area or fine particle size kaolin will require more binder than a coarse particle size kaolin. Measurement of the optimum amount of adhesive is necessary in order to get a coated surface that will not separate or pull away from the paper sheet during printing using tacky inks.

Abrasion — The hardness of particles other than kaolin in the clay can be a very important parameter because of marking on the sheet, wear on the coating applicators, and on the type used in printing. A standard test called the Valley abrasion test is available from the Technical Association of the Pulp and Paper industry. The test uses a slurry of kaolin and copper wire mesh. The kaolin slurry is circulated on the wire mesh and a micarta block is rubbed back and forth on the screen by a motorized arm for 600 cycles. The wear on the screen is measured by weight loss and is known as the abrasion value. The Georgia sedimentary kaolins have very low abrasion values.

EVALUATION TESTS FOR CERAMICS

The ceramic industry is a large user of kaolin clays in whitewares, sanitaryware, refractories, and insulators. Several tests are used to evaluate kaolins for use in ceramics. These will be described briefly.

1. Plasticity
2. Shrinkage
3. Modulus of Rupture
4. Absorption
5. PCE
6. Fired color
7. Casting rate
8. Chemical Analysis

Plasticity — Plasticity or workability is an important property and is a mesaure of the ease with which a body can be formed into various shapes. Plasticity can be measured using compression and/or tension tests which measure the resistance to deformation and the amount of deformation before cracking. The simplest analysis of plastic flow may be made from a stress strain diagram. Several tests have been designed to measure plasticity [NORTON, 1970, p. 134].

Shrinkage — Ceramic articles undergo drying and firing shrinkage during the manufacturing sequence. Linear shrinkage, i. e. the amount by which each dimension changes, is more commonly reported than volume shrinkage. The simplest way to determine linear shrinkage is to make a measurement of the dimensions before and after the shrinkage occurs. Standard size bars can be made up and dried and fired to determine the linear shrinkage.

Modulus of Rupture — The modulus of rupture (MOR) is the fracture strength of a material under a bending load. The determination of the MOR is a simple measurement and is a standard quality control test. The MOR measurement is made on a long bar of either rectangular or circular cross section, supported near its ends, with a load applied to the central portion of the supported span. The American Society of Testing Materials has standard methods for testing MOR of various ceramic materials.

Absorption — Absorption is a measure of the porosity and is usually a very carefully controlled property. The greater the porosity, the more likely will be the penetration of liquids and vapors which may cause structural damage. The American Society of Testing materials has published a set of standard test methods for porosity and absorption of ceramics.

PCE — Pyrometric cone equivalent is a measure of the combined effects of temperature plus time during the firing operation. A standard series of pyrometric cones are formulated to provide end points corresponding to reproducible amounts of heat work. Pyrometric cones are used to test the vitrification point of clays. The clay material is molded into the standard cone shape and is heated along with a number of standard cones so that its end point can be determined in terms of an equivalent cone number. This number is known as the pyrometric cone equivalent of that particular clay (ASTM method C24-56).

Fired color — This test is simple in that a small bar or a plaque can be made up and fired so that the fired color can be determined.

Casting Rate — The casting rate can vary over a wide range depending on the slip composition and the wetness and age of the mold. A reasonably fast casting rate is desirable to permit a faster mold turnover. The viscosity and thixotropy of the slip are most important in determining casting rate.

Chemical Analysis — Chemical analysis of clays is sometimes important to know particularly the iron, alkalis, and alkaline earth elements along with the aluminum and silicon content. Many ceramic properties can be related to the chemical analysis such as refractoriness, casting rate, and fired color.

RUBBER TESTS

Kaolin is used in rubber because of its reinforcing and stiffening properties and because of its low cost. Fine particle size kaolins give good resistance to abrasion and are used extensively in non-black rubber goods. The kaolins that are used in rubber contain a maximum of 1% free moisture. Other tests that are important in evaluating kaolins for use in rubber are:

1. Water Settling Characteristics
2. Oil Absorption
3. Stress-Strain
4. Tear Resistance
5. Abrasion Resistance
6. Heat Generation
7. Energy rebound
8. Extrusion and Plasticity
9. Hardness
10. Aging Characteristics
11. Water absorption

These tests are all described in detail in the book entitled Kaolin Clays and Their Industrial Uses published by the J. M. Huber Corporation of Edison, New Jersey. All these tests have a particular value in relating to certain characteristics imparted to the rubber product. For example the Water settling test gives a good idea of the reinforcing characteristics of the clay and the Oil absorption also correlates with reinforcement. The other tests listed above are run on the rubber itself after filling with the clay and require specialized equipment.

PAINT TESTS

Kaolin clays are used extensively in paints particularly in water based paint systems. Kaolin is a functional extended pigment that has good covering or hidding power, imparts desirable flow properties to the paint, and is low in cost. Standard moisture and oil absorption tests are run on all paint clays along with more specialized tests. Low moisture of less than 1% is a requirement for paint clays and oil absorption relates to a parameter call vehicle demand in the paint. The test indicates surface area and absorption in the paint system. Other tests that are run on paint clays are:

1. resistivity
2. fineness of grind
3. performance tests

Resistivity — This test is to give an index of the amount of residual soluble salts in the clay. The higher resistivity values reflect a low soluble salt content. Depending on the paint system all clays that are used have a resistivity specification because a high soluble salt content adversely affects the dispersion of the ingredients in the paint and alters certain physical properties. The test requires a conductivity bridge to measure the conductivity.

Fineness of grind — This test measures the dispersion of the kaolin and highlights the fineness of the particles. A common measurement device is the Hegman gauge which is used extensively as a control device to measure the fineness of the kaolin product.

Performance tests — Actual paint formulations are made up with all the ingredients and many measurements such as gloss, color, smoothness, flow characteristics, dispersion, stability, weathering characteristics, aging, ank many other properties are determined.

MISCELLANEOUS TESTS

Kaolins are used for many industrial applications so there are other specific tests that may be required. These woud include such tests as bulk density, surface area, various special viscosity measurements, cation exchange capacity, and many others. These tests would be prescribed by the user.

CONCLUSIONS

Kaolins are tested initially for their mineral content, particle size, brightness and color, viscosity, and pH. These tests give a good indication of the potential applications. After these potential applications are determined then evaluation for paper, paint, ceramics, plastics, rubber, and others can be made. For example if the initial evaluation indicates high viscosity then the kaolin could not be used for paper coating but if the brightness and color were good it coud be used for filling applications and perhaps ceramics. Because there are so many industrial uses for kaolin, one bad characteristic such as viscosity does not mean that it would not be a very good ceramic clay. Tests must be done, however, in order to establish its ultimate utilization.

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CORRELATION OF MINERAL COMPOSITION OF THE PARENT ROCK WITH THE MINERAL COMPOSITION OF KAOLIN

V. P. PETROV, N. D. SAMOTOIN, V. I. FIN'KO and S. S. CHEKIN

ABSTRACT

Commercial kaolin deposits are only formed from acid rock. In the weathering processes quartz grains of primary rock are conserved without any changes of size. Large kaolinite flakes arise in the place of mica by epitaxial growth on a mica sheet. Some part of iron and titanium is preserved in special minerals formed within pseudomorphs after biotite. K-feldspar changes into small newly formed kaolinite flakes. On acid plagioclase halloysite appears but on andesine-labrador montmorillonite arises. Properties of commercial kaolin depend upon all the peculiarities of the mineral transformations.

There is no doubt that relationship exists between the chemical and mineralogical composition of kaolins and the preexistent parent rocks of the kaolins. The relationship is revealed by exploitations of kaolin deposits and results of their study.

As a sufficiently well-known example one may refer to the dimensions of quartz particles in kaolins and parent rocks. The large quartz crystals are retained in kaolins formed from coarse-grained granites; beneficiation of these kaolins is performed very easily. Contrary of this, kaolins formed from fine-grained granitoids contains high quantities of fine sand and therefore beneficiation of these kaolins is much more difficult. Also one may note the kaolins in South-Eastern G. D. R. The kaolins, formed from coarse-crystalline quartz-porphyries, in the neighbourhood of Kemmlitz and Gruppensdorf, are beneficiated comparatively easily because they contain sufficiently coarse quartz, as the parent rocks do. There is the opposite situation in the small kaolin deposit at Seilitz near Meissen. Here pitchstones are developed; these rocks are almost analogous in chemistry to quartz-porphyries of previous deposits, but do practically not contain well-crystallized minerals. As a result of weathering of these pitchstones exclusively clean and homogenous kaolins were formed. These kaolins contain high quantities of fine-grained quartz, which is retained in beneficiation processes. However, these kaolins, due to their homogeneity and cleannes are used in Meissen ceramic works for the highest quality artistic porcelain wares.

In kaolins, among other minerals of the parent rocks kaolinite pseudomorphs after biotite, chloritized biotite and muscovite can be recognized very easily. The pseudomorphs after biotites are coarser than kaolinite particles; they have approximately the same size, as the biotite which was replaced, however, almost all titanium and iron of biotite are retained within the pseudomorphs and form individual minerals piercing through the kaolinite particles. These minerals form very distinctive "sagenitic lattice" in the flake.

Observations on sagenitic lattice represents the limits of possibilities of light-microscopy. Much more information about the weathering processes can be received by electron microscope. Especially interesting results were received by the method of decoration with gold [GRITSAENKO, SAMOTOIN, 1966].

Fig. 1 shows the growth of the kaolinite on the surface of cleavage plane 001 of microcline. It is very remarkable that the kaolinite crystals, consisting of few unit layers, have rhomboidal forms, and only after receiving a thickness of at least 10—20 unit layers the crystals obtain characteristic hexagonal forms. *Fig. 1* shows well the growth of the kaolinite crystals on a microcline surface in distinctive orientations. Here the main crystallographic axes a_k and b_k of kaolinite coincide with the main crystallographic axes a_m and b_m of microcline.

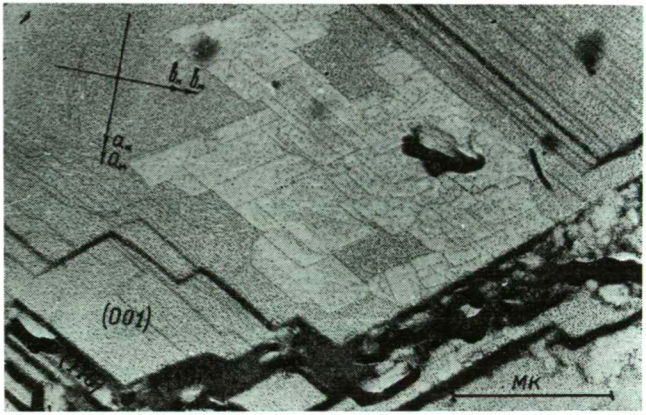

Fig. 1. Kaolinite microcrystals on the surface 001 of microcline. Arrows show directions of main crystallographic axes of microcline (a_m, b_m) and kaolinite (a_k, b_k). Weathered microcline, Eastern Siberia.

In *Fig. 2* the weathering of microcline has a progressively prograded as compared to *Fig. 1;* here the mechanism of weathering is shown well. Open surfaces of microcline have been dissolved intensively; cleavage planes are not so distinct as they are in *Fig. 1* and the etching pits are shown very well on the microcline surface. The kaolinite growing on the microcline has a large thickness and is an aggregate of many grown crystals. It is characteristic that crystals of the aggregate have almost the same orientation and hexagonal form.

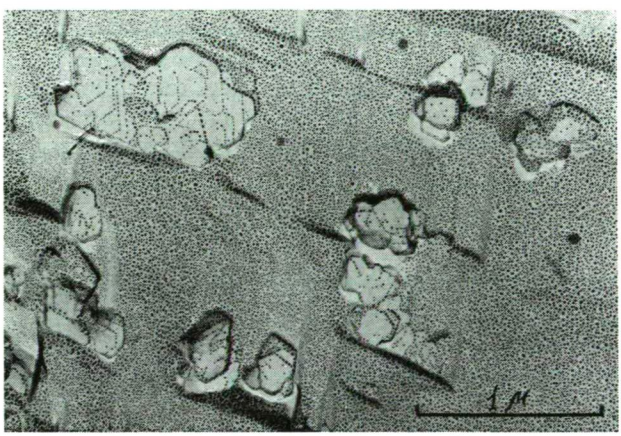

Fig. 2. "Etching pits" on microcline surface and aggregates of kaolinite crystals growing on it. Eleninskoe kaolin deposit, Ural Mts.

It is very interesting, that the influence of parent crystals, on which clay minerals have grown, is reflected in the finest details. In granitoids microcline crystals often contain albite and albite-oligoclase perthitic intergrowths. As the study of weathered perthitic intergrowths has shown they are replaced by halloysite rather than kaolinite [PETROV *et al.*, 1978]. *Fig. 3* shows the oligoclase surface on which oriented halloysite tubes have been grown. Originally halloysite, as kaolinite also, form rhomblike crystals, which, at a further stage, grow in typical tubular halloysite crsytals [CHEKIN *et al.*, 1976]. The rhomblike crystals are shown at the bases of some tubular crystals (*Fig. 3*). Halloysite nature of these rhomblike crystals has been judged with the method of selected area diffraction.

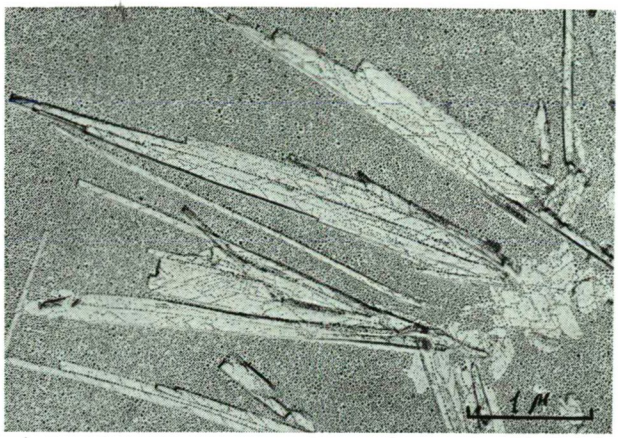

Fig. 3. Platy and tubular halloysite (7 Å?) crystals on the surface of weathered oligoclase. Soyuznoe kaolin deposits, Ural Mts.

The other clay minerals are formed on the more basic plagioclases. In the western part of Ukraine the weathering has changed the large Volynskii anorthosite massif, in which the main rock-forming mineral is andesine-labradorite feldspar (47—53% anorthite component). The first clay mineral, which has been formed by the weathering of the labradorite, is montmorillonite.

Fig. 4 shows fine sheets of montmorillonite on the cleavage surface of a labradorite crystal.

The weathering of Volynskii gabbros has been studied in detail by N. I. BUCHINSKAYA [1972]. The author has shown, that in lower section of the old crust of weathering with a thickness of more than 50 metres, montmorillonite clays are developed and they are changed upwards in kaolins. It is very interesting, that there are some alumina minerals (up to 7—10%; rarely more than 10%) in the transitional zone which is of comparatively low thickness (few metres).

The vertical change of the mineral composition of the weathering crust is also influenced by the parent rock's composition. Invariable presence of kaolinite in the upper part of the crust of weathering suggests the acid character of the superficial weathering solutions; in the lower parts of the crust of weathering the solutions have reacted with gabbros, enriched by alkaline and alkaline-earth elements and got alkalinity. As a result of this at the lower parts of the crust montmorillonite was formed, i. e. a mineral characteristic of an alkaline environment. Naturally, here a

neutral intermediate zone was formed containing gibbsite — a mineral characteristic of a neutral environment.

The authors have studied the weathered andesine-intermediate plagioclase between oligoclase and labradorite in Kazakhstan, where the crust of weathering was developed on granodiorites. Newly formed clay minerals have intermediate characteristics here. On the cleavage surface of andesine both fine sheets of montmorillonite and tubular halloysites were formed (*Fig. 5*).

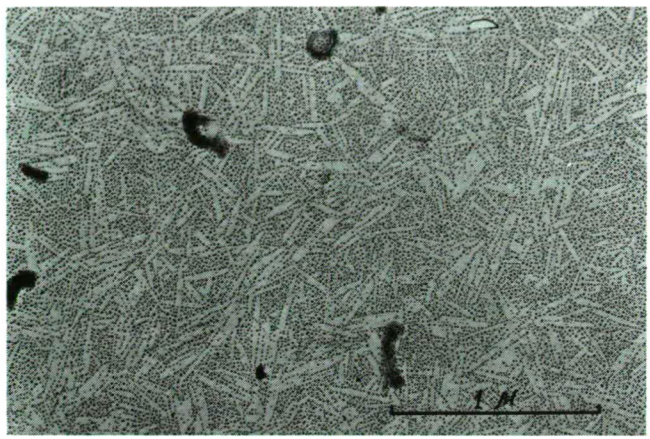

Fig. 4. Montmorillonite sheets on the cleavage surface of weathered labradorite crsytal. Golovinskoe labradorite deposit. Ukraine.

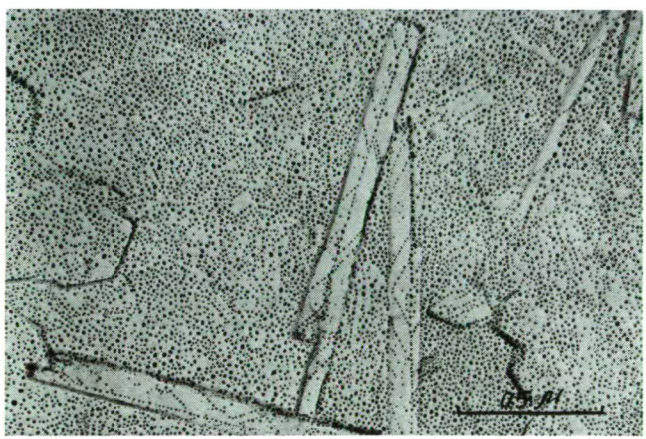

Fig. 5. Tubular crystals of halloysite (7 Å?) and montmorillonite sheets in weathered andesine. Alekseevskoe kaolin deposit, Kazakhstan.

The results of study of weathered micas are also very remarkable. It was shown, that kaolinite crystals always grow on the sheets and within the sheets of mica [CHEKIN *et al.*, 1977]. Therefore, the basic mica lattice is not preserved during the replacement of mica by kaolinite. There is only epitaxial growth of kaolinite crystals

on mica sheets (*Fig. 6*) and the dissolution of mica sheets. Therefore, a kaolinite flake, which is a pseudomorph after a mica crystal, is not a sing'e crystal but is a pseudotwin intergrowth of many fine crystals.

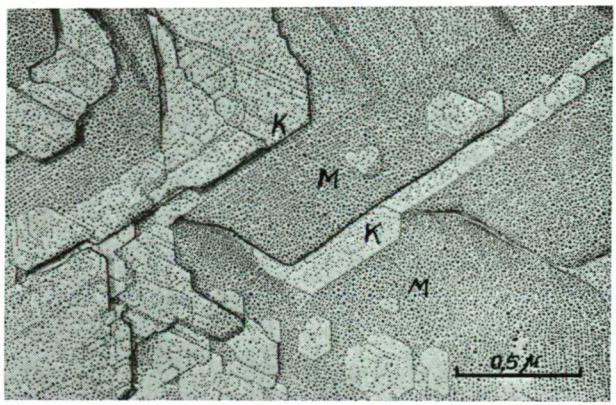

Fig. 6. Kaolinite crystals growing on the surface of muscovite crystal. Weathered sericite slate Kazakhstan.

The number of examples similar to those discussed above could be increased but even now one could see:

Firstly, the composition and properties of kaolins are controlled largely by the composition of parent rocks. Quantity of plagioclase and content of its anorthite component are factors controlling quantities of halloysite, and also often those of montmorillonite in a predominantly kaolinitic mass and, consequently, properties of kaolin such as wet strength, firing strength and melting point temperature. Ferrous admixtures in parent rocks and especially biotite content determine the colouration of kaolin and its paper filler properties.

Secondly, it was shown, that in the course of the weathering process minerals of a parent rock dissolved completely and newly formed minerals grow from a solution acting as weathering agent.

Orientation of newly formed minerals inherits often the orientation of the mineral of the parent rock due to epitaxial growth of newly formed minerals on minerals of the parent rocks.

The authors believe that the electron-microscopic method of decoration with gold is one of the most promising methods of investigation of weathering processes.

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MORPHOLOGY OF THE MAIN MINERAL COMPONENTS OF THE MÁD KIRÁLYHEGY KAOLIN

E. MOLNÁR

ABSTRACT

In this study the different microstructure of Mád Királyhegy siliceous kaolin is presented by scanning electron microscopy, X-ray diffraction and thermal analysis. The ceramic properties of this clay are influenced by the mineral composition and the different morphology.

INTRODUCTION

The Mád Királyhegy kaolin represents the characteristic type of the siliceous kaolins formed during the hydrothermal transformation of rhyolitic tuffs. Externally it is a hard, stone-like, fine-grained material in which in some places the tuff-like structure of the mother rock is preserved while in other places it contains soft centres of kaolin of a compact structure. In the holes of the preserved tuffy rock pumice embeddings and different crystalline formations can be seen. Upon touching both the tuffy and the compact structure rock are rough.

Among the main rock-forming components the following ones were determined: kaolinite, dickite, illite, allevardite, quartz and alunite. Besides the crystalline phases the rock contains a considerable amount of amorphous material, too.

Investigating the external character of the Királyhegy kaolin it can be seen that according to the enrichment of the main mineralogical components three types of rocks can be differentiated: the kaolinitic, alunitic and iron-oxidic ones. The dominant mineralogical components being present form those properties of the rock which must be considered at its utilization in the ceramic industry.

It is known that the ceramic properties of clays are decisively influenced by the morphology of the individual crystal grains forming the mineral raw material. In order to study this, scanning electron micrographs (SEM) were taken about the rock types of the recently opened Királyhegy kaolin quarry. The SEM applied in our work was of the JEOL type of the Institute SZIKKTI. — The micrographs were made by I. WOJNAROVITS.

The type of the investigated rock was determined by X-ray diffraction and thermal analyses.

KAOLINITIC TYPE OF ROCK

Fig. 1 shows the X-ray and thermal diagrams of the sample giving the data of the chemical analysis, too. According to the evaluation of the results the rock consist of 40% kaolinite, ~ 50% quartz and ~ 10% X-ray amorphous material. The morphology of the crystalline componensts of the white, compact structured, poorly peptiza-

TABLE 1

Chemical Composition (weight %)

	Kaolinitic type	Alunitic type	Iron-oxidic type
I. L.	6.57	6.60	5,30
SiO_2	72,20	59,40	74,73
Al_2O_3	16,51	17,15	16,01
Fe_2O_3	0,16	0.26	2,24
TiO_2	0.04	0,06	0,13
CaO	0,01	0,11	0,34
MgO	0,20	0,06	0,27
K_2O	0,02	3,33	1,01
Na_2O	0,01	0,04	0,03
SO_3	0,15	12,53	0,13

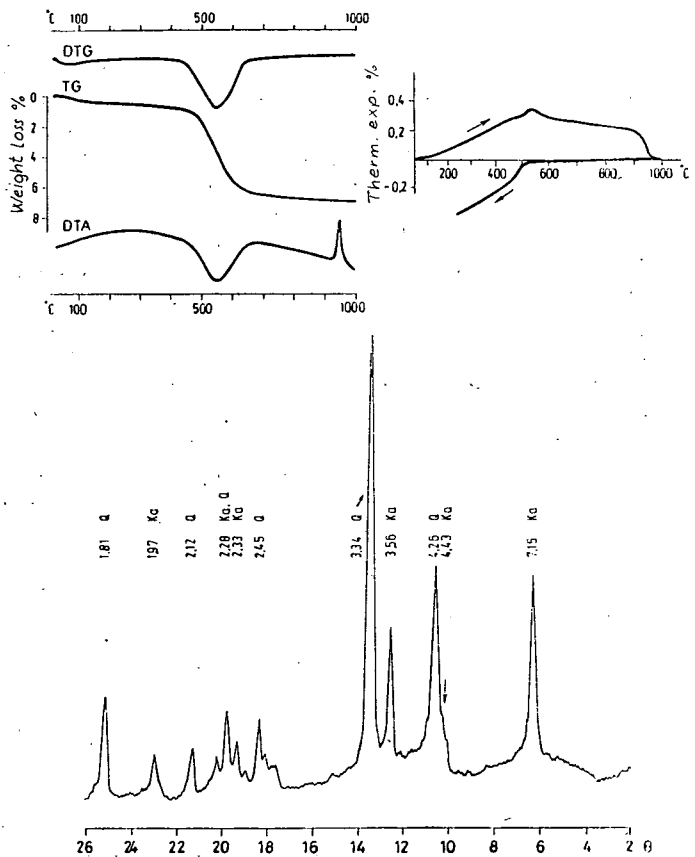

Fig. 1. X-ray diffractogram and derivatogram of a kaolinitic type rock

ble material was studied, by SEM taken of the fracture surface of the rock. On the basis of the electron micrographs two kinds of forms of appearance are characteristic of the morphology of the components of this rock:

— well-crystallized, idiomorphic crystal forms;

— grain aggregates formed of small crystal detritus.

The morphology presented in the picture *(Fig. 2)*) is a classical example of the individual crystal grains of the well-crystallized, idiomorphic kandite-minerals. Pseudohexagonal crystal forms of larger and smaller size can be seen among which the larger ones have an edge length of 1—2 μm. It can be observed that the idiomorphic crystals of this size consist of flakes adhered together. This can well be seen on the

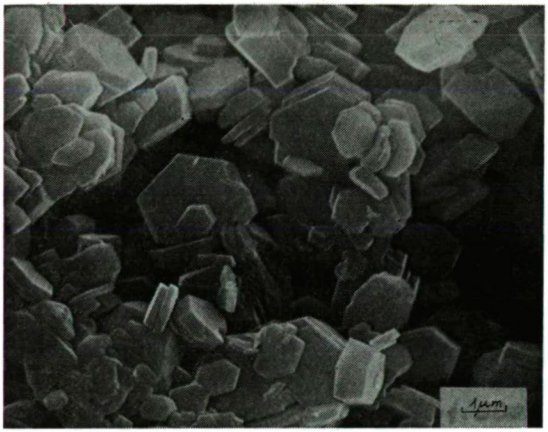

Fig. 2. Morphology of the individual crystal grains of idiomorphic kandite minerals

fracture surface of the large crystal positioned in the middle of the picture and on the other crystal as well, where the thin flakes are a bit slipped on one another. The idiomorphic grains of smaller size are apparent by their thickness. This thickness varies between 0,1 and 0,5 μm. It is conspicuous that hexagonal crystal grains flanked by trapeziform sides can be observed in more places in which the dickite can be identified. Besides this the micrographs show large quartz crystals wedged in between the kandite minerals.

The picture shown in *Fig. 3* is typical of the other form of appearance of the crystalline components of the kaolinitic type rock. Here no regular, idiomorphic crystalline forms can be seen but only the smaller of larger grain aggregates formed of the debris of the crystal. At the same time, however, the pseudohexagonal forms can be recognized on these broken grain aggregates.

Ceramic industrial technological investigations showed that this kaolinitic rock of detrital morphology has a larger shrinkage and can be fired into a more compact material than the rock presented earlier.

ALUNITIC TYPE OF ROCK

The investigated alunitic rock sample originated from the SW workface of the kaolin quarry where it has been locally accumulated in large quantities at the time of sampling. *Fig. 4* shows its X-ray diffraction pattern and thermal curve as well as its

chemical analysis. According to the data the mineralogical composition of the rock is the following: 15—20% kaolinite, 30% alunite and 40—45% quartz and X-ray amorphous material. The external appearance of the alunitic type of rock is char-

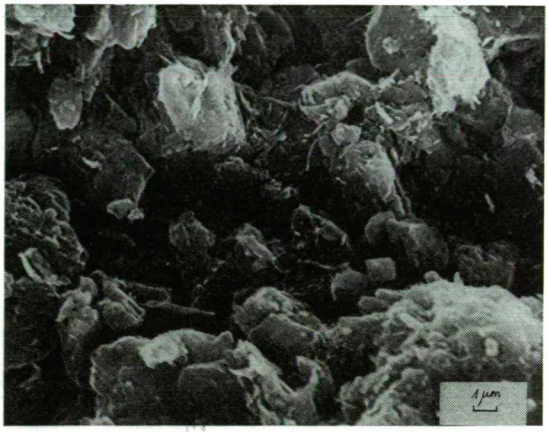

Fig. 3. Grain aggregates formed of the debris of crystals

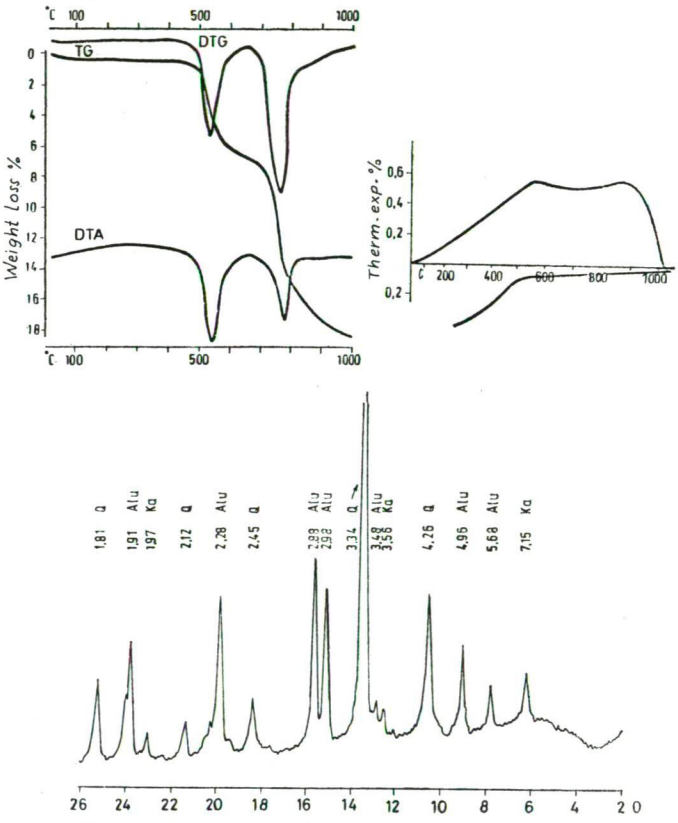

Fig. 4. X-ray diffractogram and derivatogram of an alunitic type rock

acterized by greyish-white, pink and yellowish colour and a hard, stone-like, strongly cemented, porous tuffy structure. In the voids of the tuff the alunite forms druses while in the mother rock it is finely distributed. The morphology of the mineralogical components of this type of rock can be studied in *Fig. 5*. The alunite being present

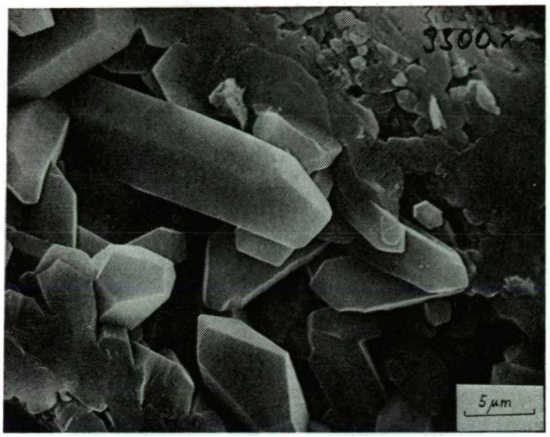

Fig. 5. Morphology of alunite and quartz crystals

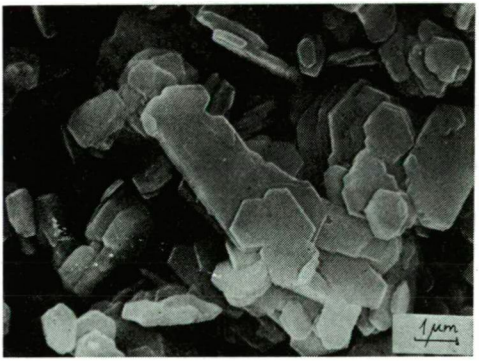

Fig. 6. Morphology of the kandite minerals being present in the alunitic type rock

in large quantities can be recognized in forms flaked by pentagonal sides. The quartz can be seen in long, columnar forms. — At the same time, in this type of rock also the kandite crystals having well-crystallized idiomorphic shape can be found, see *Fig 6*. The morphology of the well-crystallized kaolinite and the dickite crystals thickened in the direction of the „c" axis can be observed. On the basis of its morphology the alunitic type of rock, like the former one, cannot be peptized and plastically formed. Due to the high alunite content it cannot be utilized as a ceramic raw material.

IRON-OXIDIC TYPE OF ROCK

The X-ray pattern and the derivatogram (*Fig. 7*) are quite similar to those that were made of the kaolinitic rock samples. The mineralogical composition of the rock is the following: 40—50% clay-mineral, 45—50% quartz and 10% X-ray amor-

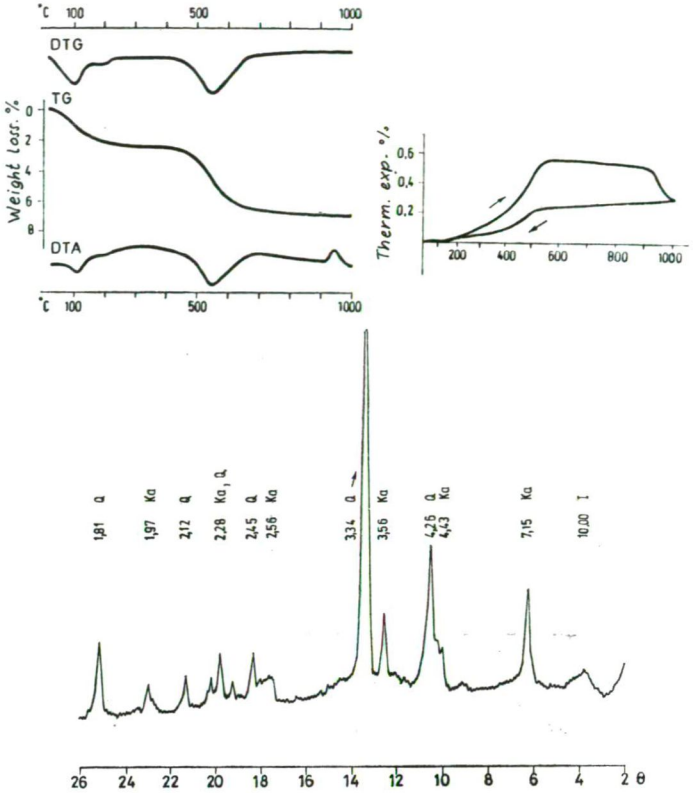

Fig. 7. X-ray diffractogram and derivatogram of an iron oxidic type rock

phous material. This type of rock has an earthy appearance but is of good strength, the tuffy structure is mainly preserved and greenish clay-mineral centres are accumulated in the voids of the rock. Although this rock has been differentiated due to its reddish-brown colour originating from the iron-oxide, the main difference to the

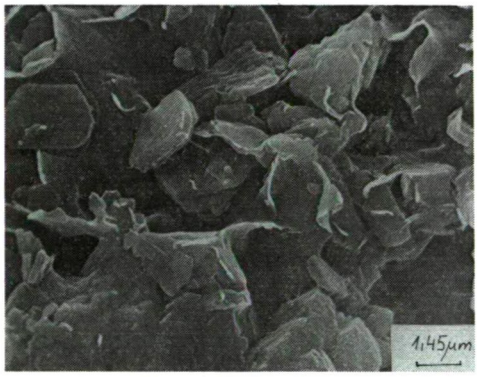

Fig. 8. Broken kandites embedded into a plastic material

kaolinitic type of rock lies in the composition of the accumulated centres of clay-minerals. The micrographs *(Fig. 8)* made of the fracture surface of the rock show that the kandites becoming distinct by well-crystallized, definite edges and characterizing the kaolinitic type are missing here. There are kaolinite and dickite crystals but these are mainly broken edged and embedded into some kind of material that seems to be velvety.

In the next picture (*Fig. 9*) columnar kaolinite, a crystal formation of very interesting habit can be seen, the elongated figures in the background remind of illite.

In the time of the geological research from this material also the allevardite was determined. — In order to get a better knowledge of the morphology of allevard-

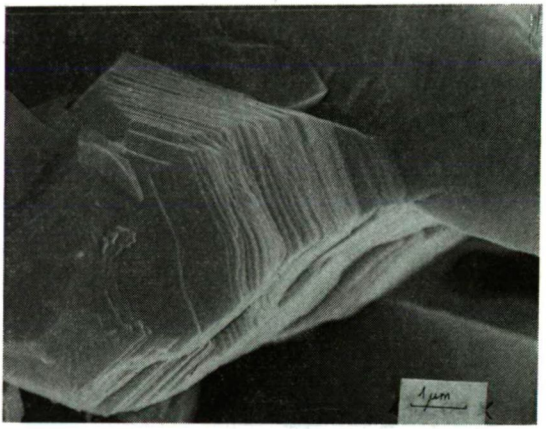

Fig. 9. Kaolinite crystals of columnar development

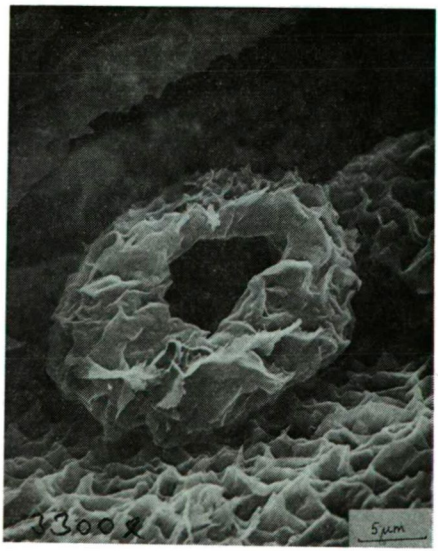

Fig. 10. Morphology of a prepared clay mineral specimen containing allevardite

ite the prepared part was dispersed in water and SEM were taken of the fine particles. The image appearing on the screen caused a real experience to the spectators. See here picture about the most interesting sample *(Fig. 10)*. In this picture thin, slightly transparent, strongly slashed, twirledly edged, frayed aggregates forming bands and nests can be seen. Their surface is sensibly soft like a velvet. These do not possess idiomorphic-crystal forms. It is, however, worthwile to observe that there is an individually large size kaolinite crystal aggregate settled into the voids placed between the bands.

The next picture also was taken of the fracture surface of the specimen, see *Fig. 11*. Here again nice kaolinite crystal aggregates can be seen. The interesting point

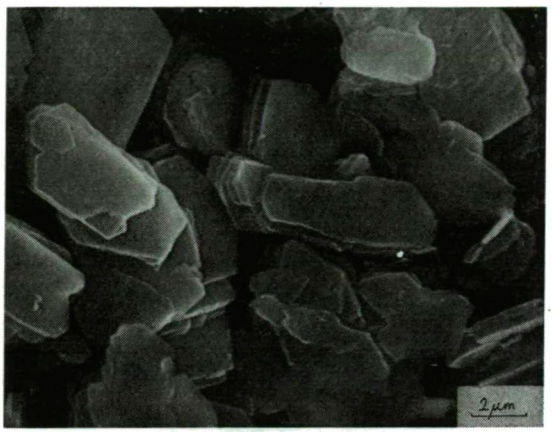

Fig. 11. Crystals formed at the broken edges of kaolinite

of this picture is — what could already be seen in more pictures — that one corner of the crystal is broken and due to this the sides are a bit sloped and smaller crysta, aggregates are settled into this spot. I show this picture with a higher magnificationl too, with the intention to make the experts dealing with the genesis of kaolins give a possibly explanation of this phenomenon.

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CHARACTERIZATION OF KAOLIN MINERALS OF DIFFERENT ORIGIN

(essentially from Hungarian deposits)

É. KOCSÁRDY and A. HEYDEMANN

ABSTRACT

Kaolinite minerals from weathered rhyolite tuffs, from sedimentary kaolin clays, bauxites and argillaceous lignites were studied by X-ray diffractographic, infrared-spectroscopic and thermoanalytic methods. In addition to determining the mineralogical composition and the grain size distribution of bulk samples, the authors obtained closer characterization of various kaolinite minerals by measuring the polytypes and the crystallinity state of the minerals. X-ray diffractography was used for assessing the Hinkley index and the half-width of the 001-reflection, while infrared techniques were resorted to for assessing, among other things, the K_1-index ($K_1 = E_{3695\ cm}{}^{-1} / E_{3620\ cm}{}^{-1}$) and the K_2-index ($K_2 = E_{3670} + E_{3650} + E_{3620}/E_{3695}$).

All these results should be relied on for attempting to distinguish between kaolinites of different genesis.

INTRODUCTION

The various kaolin deposits of Hungary have already been studied mineralogically by many authors [among others: NEMECZ, 1973; MÁTYÁS, 1974]. According to these investigations some of the deposits were formed by postvolcanic activities, others by nearsurface weathering processes. Consequently, the kaolin minerals occurring in these deposits must have been formed under different physico-chemical conditions. The question is whether the differences in the genetic processes are anyhow reflected in the structure of the kaolin minerals, their polytypes or the degree of stacking.

VAN DER MAREL and KROHMER [1969] examined the crystallinity of kaolinites, fireclay minerals and ball clays of various deposits by means of X-ray and infrared spectroscopic method. They found the degree of stacking to vary widely within each group, but they did not discuss whether differences in the genesis were responsible for this. KATO and KANAOKA [1978] while studying Japanese kaolins by means of special infrared spectroscopic techniques did succeed in differentiating between kaolinites of hydrothermal and weathering origin on the basis of their different structure. But their samples came from a restricted area.

Aim of the present work was therefore to examine to what extent differentiation between kaolin minerals of different origin and mode of occurrence is really possible.

EXPERIMENTAL

Methods

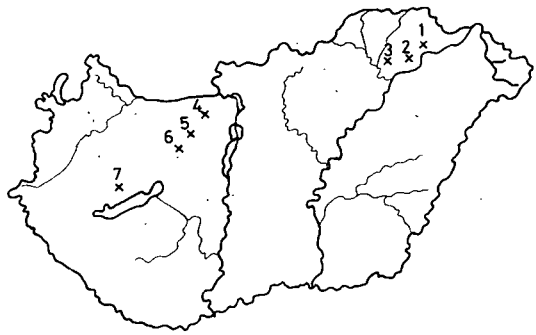
The kaolin samples were fractionated after ultrasonic treatment into the fractions $< 2\ \mu\ \varnothing$, $2-63\ \mu\ \varnothing$ and $> 63\ \mu\ \varnothing$. X-ray diffraction analyses of oriented and randomly oriented samples were made with CuKα radiation and X-ray fluorescence analyses with W-radiation.

A Perkin Elmer grating IR spectrometer 457 was employed for IR-analyses using the KBr-pellet technique. Thermogravimetric analyses were made with a Mettler TA—1 Thermal Analyzer (heating rate: 10°/min, TG: 100/10 mg).

The mineralogical composition of the samples was determined by X-ray, IR- and thermoanalytic techniques [KOCSÁRDY, 1978; FLEHMIG and KURZE, 1974].

Material

Samples of various kaolin deposits from all over Hungary were investigated. In *Fig. 1* locality, mode of occurrence, genesis and mineral composition of the samplex are listed. Six samples from the Tokaj Mountains were selected as examples for hydrothermal kaolin formation. The deposits were formed predominantly in Sarmatian time by postvolcanic processes. Main source rocks were rhyolites. Kaolins



Sample	Localities	Occurrence	Genesis	Mineral composition
1 KSZ	Szegilong / Tokaj M.	kaolin	hydroth.	
KBO	Bomboly / "	"	"	
2 KKP	Királyhegy / "	"	"	
KKD	Királyhegy / "	"	"	
3 KDR	Rátka / "	"	"	
KBR	Rátka / "	"	"	
5 B 16	Tatabánya	with	weath.	
B 41	"	brown	+	
B 42	"	coal	diagen?	
4 KS	Sárisáp / Visegrád	kaolin	weath.	
6 KBG	Gánt	in	weath. + diagen.	AL—HYDR.
7 KBH	Halimba	bauxite		n. d.

kaolinite quartz illite smectite other min. coal

Fig. 1. Kaolin samples from Hungary compared to one another regarding locality, genesis and mineral composition

occur partly as primary deposits but also sedimentary kaolins are present in the nearby basins. Their material was mainly derived from the primary deposits in the surroundings. Kaolin minerals and quartz are the major components, smectites, amorphous silica, volcanic glass and alunite occur occasionally. Three samples were collected from the Eocene brown coal basin of Tatabánya. These are carbonaceous clays to clayey lignites. The mineral assemblage shows kaolin minerals as major component together with quartz, illite and illite-chlorite mixed-layer minerals. Investigations of the carbonaceous matter exhibits varying degrees of coalification, notably sample B42 is most strongly coalified.

According to VARJÚ [1966] the kaolins of Sárisáp were formed by weathering processes probably involving organic substances derived from the overlying lignite seams.

The kaolin minerals occurring in the bauxites of Gánt and Halimba are believed to provide additional examples for non-hydrothermal minerals. But from the geological setting it cannot be decided whether they are formed by weathering or diagenetically by re-silicification of aluminum hydroxides.

In addition to this Hungarian material samples of other deposits were also analyzed (*Fig. 2*). The kaolin of Wolfka (GDR) resulted from weathering of porphyry rocks, those from Karlovy Vary and Sedlec (Zettlitz, Czechoslovakia) from granites and at Horny Briza arkoses were subjected to weathering. From similar source rocks the kaolin of Georgia (USA) is derived. The kaolin of Keokuk (Iowa, USA) originated from geodes.

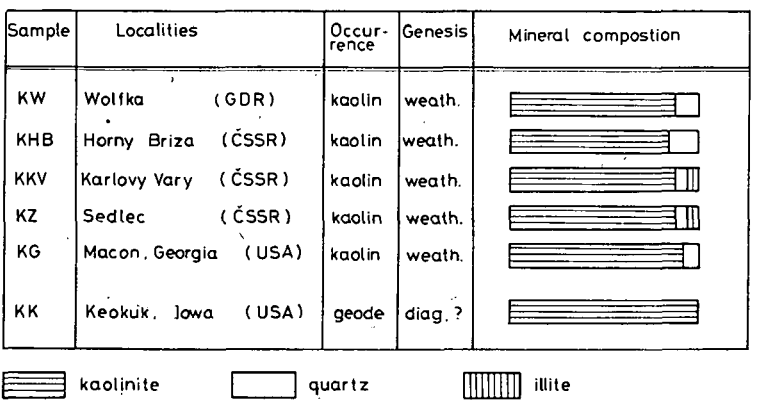


Fig. 2. The investigated kaolin samples from Europa and the USA and their mineral composition

Characterization of kaolin minerals

Mainly X-ray methods and IR spectroscopic techniques were chosen for the characterization of the kaolin minerals.

X-ray diagrams from randomly oriented samples were used for the determination of the Hinkley index, H_i [HINKLEY, 1963]. Its determination is shown schematically in *Fig. 3*. This index H_i, the crystallinity index, gives an estimation of the extent of stacking imperfections. The values for H_i vary between zero for poorly crystallized kaolin minerals and 1.6 for very well crystallized kaolinites.

X-ray diagrams of oriented samples were used to determine the peak width of the (001)-reflection at half height *(Fig. 3)*. TRUNZ [1974] found a striking correla-

TABLE 1

IR-characteristics of kaolin minerals
(K: extinction ratios see Fig. 4)

	Polytype		n_{OH}	K_1	K_2	K_3
kaolinite-D	T_d	monoclinic	3	1.1—1.5	—	>1.4
kaolinite	1T	triclinic	4	1.0—1.7	1.4—2.2	—
dickite	2M	monoclinic	3	0.5—1.1	—	1.5

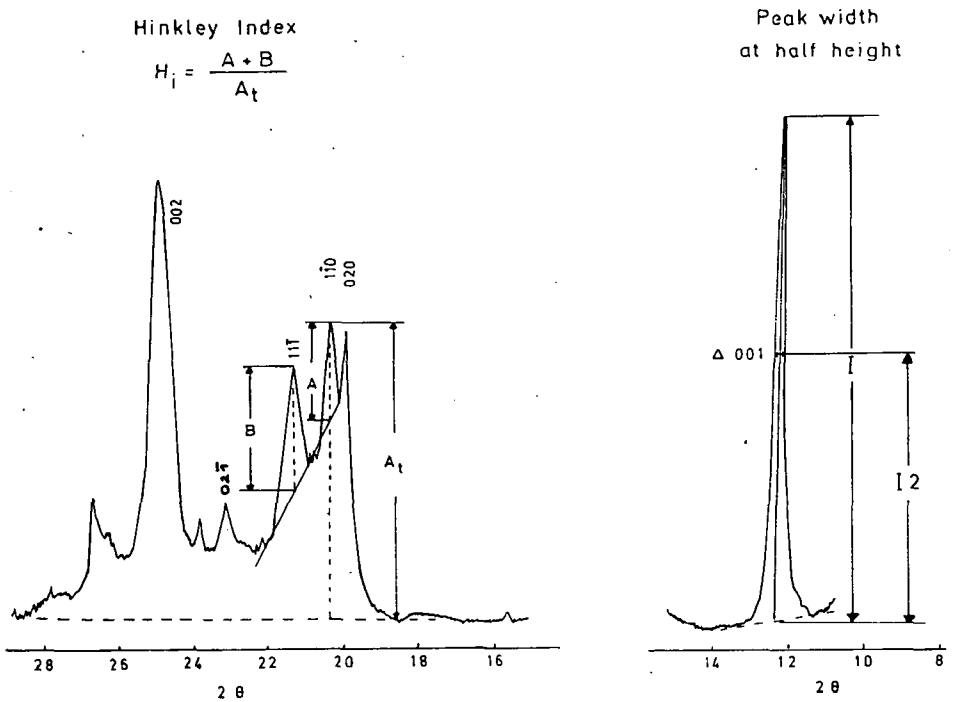


Fig. 3. Definition of the Hinkley index (H_i) and the measure of half-width of the 001 line

tion between the Hinkley index and this width at half height. But he admitted that from a crystallographic point of view an increase in the broadening of the (001) peak with increasing stacking imperfections (decreasing crystallinity) does not seem plausible.

The IR spectra in the region of the OH-stretching vibrations (3700—3500 cm^{-1}) provided primarily information on the kaolin polytype present in the sample. The number of absorption bands (n_{OH}) together with the extinction ratio of the two strongest bands (at 3695 and 3620 cm^{-1}) were used for the differentiation between T_d kaolinite, 1T kaolinite and dickite (Table 1, *Fig. 4)*.

But also information on the crystallinity of the various minerals were derived from the IR spectra. Already PARKER [1969] used the ratio Å 3695/Å 3620 for the

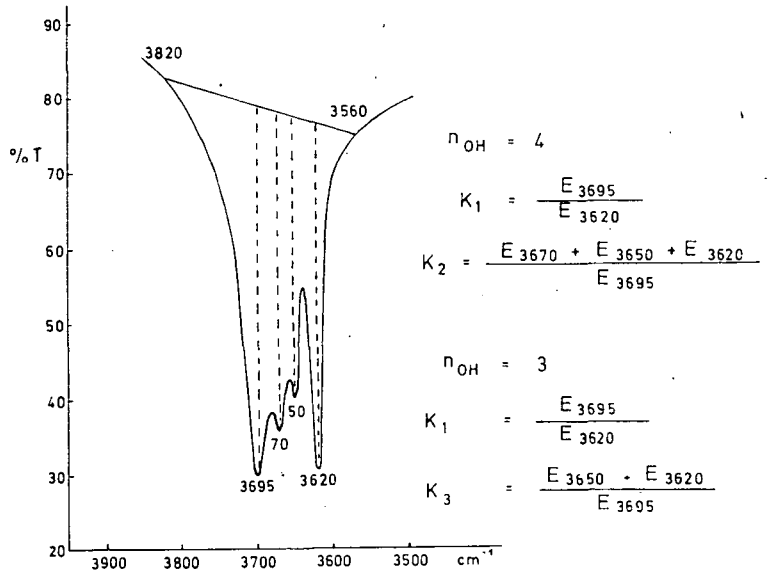


Fig. 4. Calculation of the crystallinity index from IR spectra at $n_{OH}=4$ and $n_{OH}=3$

characterization of kaolinites and discovered a relationship between the crystallinity. index H_i and this ratio.

Here the extinction ratios K_1, K_2 and K_3 were introduced. Definition and calculation of these terms are shown in *Fig. 4*. Only a very vague relationship between crystallinity index H_i and the extinction ratios could be detected.

RESULTS AND DISCUSSION

The preliminary results of this investigation are summarized in Table 2. Polytype, K-values, peak width (Δ 001) and crystallinity index H_i of the kaolin minerals together with grain size distribution of the samples are listed.

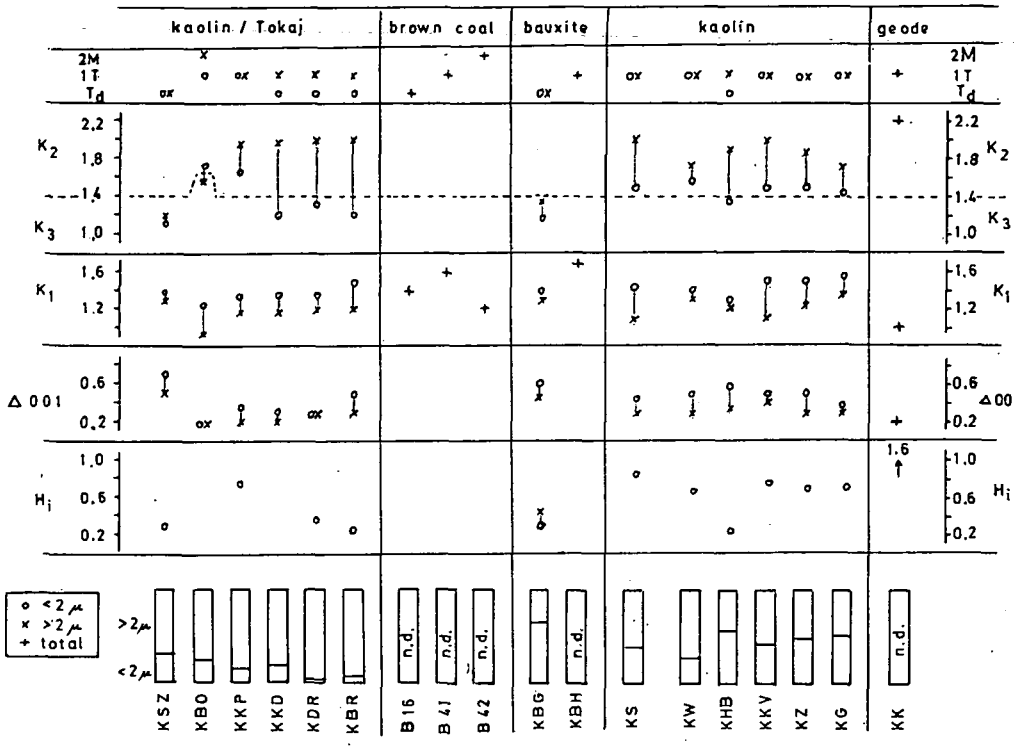
Most striking is the fact that there are samples which contain two kaolin polytypes side by side, for example T_d kaolinite in the $<2\,\mu$ fraction and 1T kaolinite in the $>2\,\mu$ fraction.

Kaolin clays consisting of mixtures of kaolin polymorphs have been described by KELLER [1967, 1978], who used electron optical methods. From X-ray analyses no such informations are available. Crystallinity indices can be obtained from the diagrams. But, it is impossible to decide whether the crystallinity represents an "apparent" one, derived from a mixture, or is the "true" crystallinity of a single kaolin polytype.

Also IR spectra are not conclusive, in general. In *Fig. 5* data from artificial mixtures of well crystallized 1T kaolinite and poorly crystalline T_d kaolinite (both $<2\,\mu\,\varnothing$) are presented. With increasing admixture of the T_d component the K_2 value decreases. In a monomineralic sample this would mean decreasing crystallinity. But here the value of K_2 depends exclusively on the composition of the mixture. It is also noteworthy that even in mixtures containing 70% of the T_d kaolinite, still the 1T polytype is predominant (in the OH-region of the IR spectra four bands are recorded).

TABLE 2

Polytypes, extinction ratios K_1, K_2, K_3 peak width at half height ($\Delta 001$) and Hinkley index H_i from the kaolin minerals present in the samples studied, in addition the grain size distribution



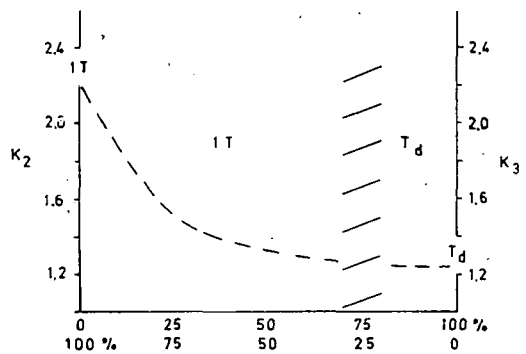


Fig. 5. Change of the crystallinity indices in 1T and T_d kaolinite mixtures

For the interpretation of the data in Table 2 these observations are of some importance. In samples, where IR analyses revealed two polytypes, all data are very likely only "apparent" ones, resulting primarily from the mixture of the two components. Differences between the grain size fractions can therefore exclusively be explained by changes in the composition of the mixture, for example T_d kaolinite

predominant in the $<2\ \mu$ and 1T kaolinite in the $>2\ \mu\ \varnothing$ fraction. But also variations in the properties of a single polytype with grain size may add to these differences. In samples where IR analyses revealed only one polytype, still two or more may be present. This can be demonstrated with a kaolinite from China. Electron optical studies indicated the presence of at least two polymorphs (pers. communication of Prof. KELLER), while the IR spectra and X-ray diagrams of both size fractions were almost identical, thus giving no hint to the presence of more than one polytype in this sample. These observations have to be considered further.

A first attempt of differentiating between kaolin minerals of different genesis was made by checking the influence of the environments on the formation of kaolin polytypes. All three, T_d kaolinite, 1T kaolinite and 2M dickite do occur in both hydrothermal and weathering-diagenetic environments.

The 2M polytype (dickite) was found, however, only in a few samples from the Tokaj territory and the Tatabánya coal basin. The dickite from the Tokaj Mountains came from zones directly adjacent to points of hydrothermal exhalations. Here hydrothermal genesis seems to be certain. The dickites from Tatabánya were found in those parts of the brown coal deposits where coalification of the surrounding lignites was the highest. It is assumed that these deposits were for some time locally subjected to higher temperatures. Under favourable conditions coalification coupled with alteration of pre-existing kaolin minerals into dickite must have taken place. Alteration of poorly crystalline kaolin minerals into dickite during high grade diagenesis was already described by SHUTOV [1970]. The presence of dickite consequently does not imply the conclusion of hydrothermal origin, but elevated temperatures apparently seem to be necessary.

The two kaolinite polytypes, 1T and T_d, have for a long time been known to occur in both the hydrothermal as well as in the weathering domains [SUDO and SHIMODA, 1978, among others], a fact also confirmed by the data presented here.

As far as the Hinkley index H_i and the K-values are concerned, similar variations are observed independent of the origin of the kaolin minerals.

Summarizing all the observations it can be stated that kaolin minerals of the same polytype and crystallinity occur in deposits formed under very different conditions. On the other hand different polytypes were observed side by side in deposits supposedly formed by the same process.

Already KELLER [1977] emphasized the importance of the geochemical environment for the formation of the various kaolin polytypes or polymorphs under weathering conditions. Also for hydrothermally formed kaolin minerals the geochemical parameters seem to be significant. This resulted from chemical and mineralogical investigations of kaolin samples from the Tokaj Mountains (Table 3).

The poorly crystalline T_d kaolinite from Szegilong (KSZ) is rich in iron, while the well crystallized 1T kaolinite from Bomboly (KBO) contains only very little iron in the structure. Similar relationships between iron content and crystall were also observed by MESTDAGH *et al.*, [1980].

Not only variable iron content, but also variation of the zinc concentrations emphasize differences in geochemical environment during mineral formation. Although KÖSTER [1969] stated that the trace element of kaolin minerals is largely determined by the source rock, in the Tokaj area certainly both, composition of the hydrothermal solution and source rock (mainly rhyolitic tuffs) were important geochemical parameters.

KELLER [1977] called also attention to the possiblity of changes of the primarily formed kaolin minerals by diagenetic processes, particularly in older kaolin deposits.

To what extent such diagenetic alterations changed already the primary composition of the kaolins studied here is difficult to say. The formation of dickite in the brown coals from Tatabánya were explained by such processes.

TABLE 3

Iron, zinc and kaolin mineral content in the <2 μ fraction of samples from the Tokaj area (samples were treated with buffered sodium dithionite solution for removal of iron oxyhydrate coatings)

Sample	Kaolin min. content	Polytype	Fe %	Zn ppm
KSZ	>95	T_d	4.9	500
KKP	>95	1T	1.6	150
KBO	90	1T+2 M	0.3	240

Considering all the observations and data it seems very unlikely that differentiation between kaolin minerals of different origin should be possible if it is based exclusively on investigations of crystal structure, polytype or crystallinity as determined by X-rays and IR spectroscopy. Even if all available data from geological, chemical, mineralogcial analyses are considered in addition, differentiation seems still to be rather difficult.

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PHOSPHATE MINERALS WITH RARE ELEMENTS IN KAOLINS

K. SZPILA and P. DZIERZANOWSKI

ABSTRACT

Geochemical investigations of the primary and secondary kaolins from the Lower Silesian deposits yielded the unusually high contents of Pb, Sr and Ba as compared with the other trace elements. Concentrations of Pb, Sr and Ba sometimes reach values over 1000 g/t. Maximum contents of those elements in the secondary kaolin from the deposit Maria III were found in the grain class $<2\ \mu m$, whereas in the primary kaolins developed both from the Strzegom and Strzelin granitoids often two different grain classes of each sample of kaolin bear high concentrations of Pb, Sr and Ba.

An attempt was made to determine the mode of occurrence of those elements, using the transmission electron microscopy and electron microprobe method.

Single grain preparations and their replicas obtained by the controlled etching of kaolins with hydrofluoric acid were applied for electron microscopy. In addition to the main minerals easily dissolving in HF (kaolinite, quartz, micas) and accessory ones resistant to the etching (anatase, rutile), the third kind of grains was found, being etched only in part. The latter were analysed by electron microprobe method. The obtained spectra bear intensive excited X-ray radiation with wavelengths typical of Al, Pb, Sr and P, and moreover, sometimes weaker radiation of Ce, La, Ba and Ca.

Analysis of the chemical composition and characteristic morphological features of the studied grains proved that in the fine grain classes of kaolins commonly there occur minerals from the groups goyazite $SrAl_3[(PO_4)_2(OH)_5]\cdot H_2O$ and plumbogummite $PbAl_3[(PO_4)_2(OH)_5]\cdot H_2O$.

Chemical composition of the individual grains of the discussed mineral groups, all derived from the same kaolin specimen, suggests that strontium and lead may replace diadochically one another, resulting in the series of solid solutions, with a participation of phosphate molecules bearing La, Ce, Ba and Ca.

INTRODUCTION

The kaolin deposits occur in Poland mainly in the area of Lower Silesia. They are genetically associated with the weathering processes of the rocks of the crystalline substratum. The most valuable deposits of primary kaolins are developed on the granitods and gneisses of the Strzelin and Strzegom area (the Bolesławice and Wyszonowice deposits). Weakly compact kaolinite sandstones of Santonian age in the Bolesławiec basin (the Maria III at Nowogrodziec and Zofia at Czerwona Woda) are secondary deposits and are of great economic importance.

The main minerals of kaolins i. e. kaolinite, quartz and micas occur in all kaolins but in variable proportions what depends on the origin of the deposit. Beside of the above minerals there are many subordinate ones in the Lower Silesian kaolins. Those are feldspars, secondary micas, chlorites, smectites, iron carbonates and iron sulphides, iron oxides and titanium oxides and sometimes also unaltered accessory minerals of parent rocks such as zircon, titanite, apatite, epidote etc. (WIEWIÓRA, 1973, STOCH, SIKORA, 1975, SZPILA, 1976a].

Secondary minerals of the kaolins are not satisfactorily recognized as concerns mainly small grains (of the order of 1 μm), that are difficult to separate and identify by classical methods of phase analysis. Their kaolin content is small but during the enrichment process of the kaolins they concentrate in the smallest fractions and negatively influence the quality of the kaolin raw materials. These minerals carry many elements that colour the kaolins and make their whiteness worse [SZPILA, 1970, 1973, 1976a, 1976b].

An attempt is undertaken in the present paper to identify the accessory minerals occurring in the smallest fractions of various kaolins and to determine the form of their occurrence. Samples of primary kaolins from the Bolesławice and Wyszonowice deposits and of secondary kaolins from the Maria III and Czerwona Woda deposits have been chosen for the examination. The fine fractions of those samples are characterized by increased content of Fe, Ti, Pb, Sr, Ba and other elements. These fractions were carefully studied under the electron microscope and the selected grains were analysed by microprobe method [SZPILA, DZIERZANOWSKI, 1978]. Suspension preparates and replicas obtained from suspension preparates after previous etching in HF have been used in electron microscopic studies. The observations were carried out using the Tesla BS 613 transmission electron microscope and the microprobes — analysis using the JEM—1000 microscope equipped with electronic X-radiation spectrometer of Link system with semiconductor detector Si(Li). In order to identify the accessory minerals morphologic features of the particular grains were used as well as their resistance to etching by HF, the results of microprobe analyses, and in some cases also the electron diffraction images obtained from grains that were partly etched. Some samples were enriched in heavy minerals by flocculation method and the obtained concentrates were then analysed by X-ray diffractometer.

RESULTS OF INVESTIGATIONS

The Lower Silesian kaolins differ considerably in their Fe and Ti content. In various deposits and even in various samples from the same deposit the Fe — Ti proportion in the particular grain fractions varies. The Fe_2O_3, FeO and TiO_2 content in the selected grain fractions of the primary and secondary kaolins is given in Table 1. A tendency to increase of Fe and Ti content with decreasing grain diameter is very remarkable in secondary kaolins which is a general phenomenon. This pertains also to the primary kaolins but in many samples there are some deviations from that rule which is expressed by two maximas of the Fe and Ti concentration [WIEWIÓRA 1973, SZPILA, 1976a]. This proves that both elements occur in at least two various mineral forms. In the kaolin from the Maria III deposit Fe occurs in form of fine, oval grains of diameter less than 0.1 μm bound in chain-like concentrations (Plate I/1). Microprobe analyses of those concentrations proved that those are oxides as asides of very strong bands of X-ray radiaton of iron there were only weak maximas of Si, Al, and Mn that are due to impurities *(Fig. 1a)*. In fine fraction of the primary kaolin from the Bolesławice deposit the presence of iron has been stated in form of isometric sulphide grains resistant to HF (Plate I, 2. *Fig. 1b*). Titanium minerals are relatively easily recognizable under electron microscope which pertains mostly to most common in kaolins anatase and rutile because of their characteristic idiomorphic shapes and total resistance to HF (Plate I, 3, 4, 5, 6). Microprobe analysis of those grains shows that these are titanium oxides with insignificant admixture of iron *(Fig. 1c)*.

TABLE 1

Content of the iron and titanium in the Lower Silesian kaolins (weight %)

Deposit; number of the sample, fraction in μm	Fe_2O_3	FeO	TiO_2	Total
Bolesławice				
1. <2	0,75	0,32	0,09	1,17
2—5	0,96	0,05	0,08	1,09
2. <2	2,44	0,30	0,08	2,82
2—5	1,77	0,14	0,09	2,00
Wyszonowice				
1. <2	1,43	0,09	0,79	2,31
2—5	1,79	0,07	1,10	2.96
2. <2	1,34	—	0,25	1,59
2—5	1,15	—	0,67	1,82
Maria III				
1. industry washed sample	0,57	—	0,58	1,15
Czerwona Woda				
1. <30	0,86	—	0,61	1,47
30—60	0,44	—	0,46	0,90

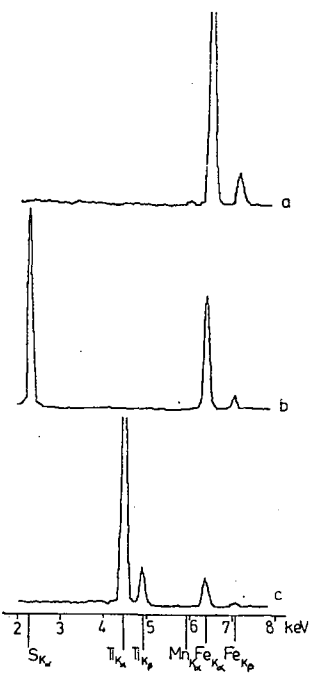

Fig. 1. X-ray images of accessory minerals of the kaolins
a) iron oxides in the Maria III kaolin (grain presented Plate I, 1),
b) iron sulphide in the Boleslawice kaolin (grain presented on Plate I, 2),
c) anatase in the Maria III kaolin (grain presented on Plate I, 3)

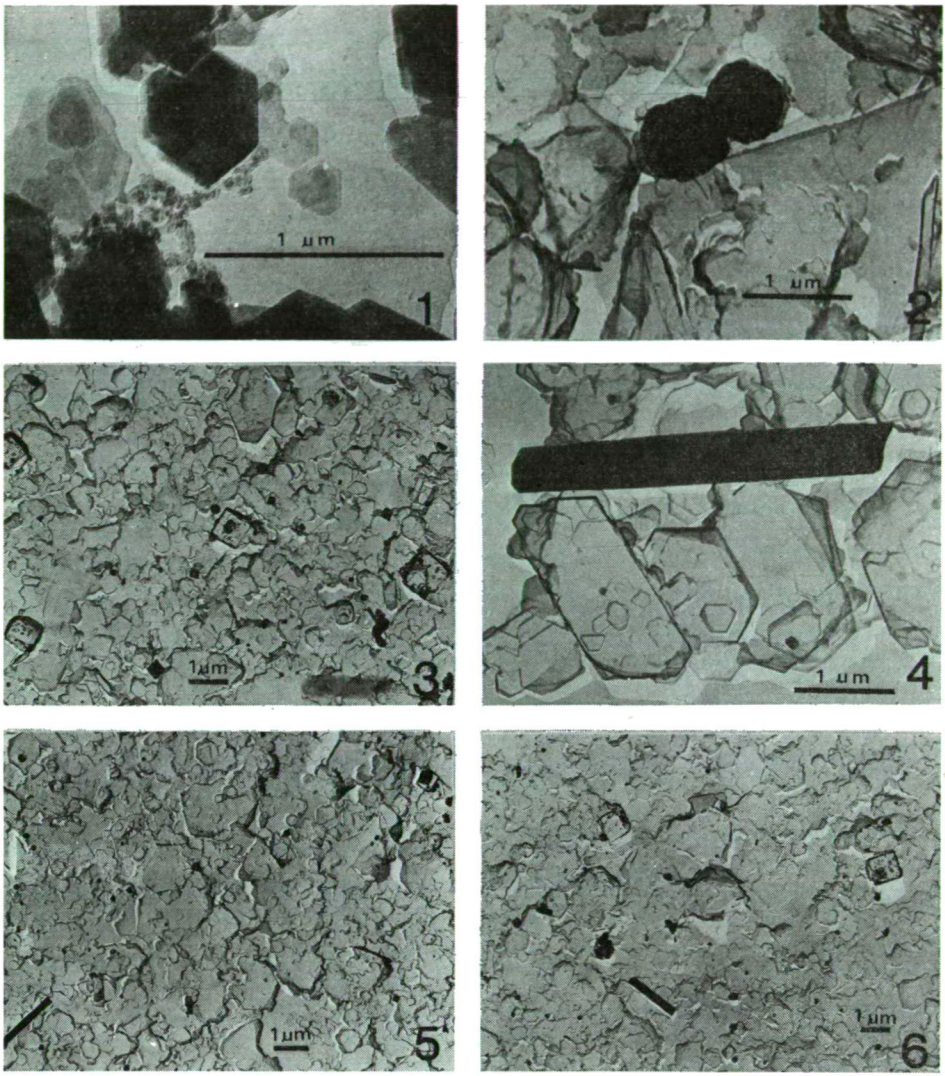

PLATE I

1. Maria III kaolin. Fine concentrations of iron oxides against the background of kaolinite flakes (suspension)
2. Bolesławice kaolin. Iron sulphide among the kaolinite flakes (replica)
3. Maria III. kaolin. Kaolinite, anatase, phosphates (replica)
4. Maria III kaolin. Rutile grain (replica)
5. Maria III kaolin. Kaolinite, mica, phosphates,, anatase and rutile (replica)
6. Maria III kaolin. Kaolinite, mica, phosphate, anatase, rutile (replica)

Presence of many trace elements has been stated in the Lower Silesian kaolins. Their forms of occurrence are not known so far, although they may influence the colour and whiteness of the kaolins [SZPILA, 1976a, b]. Those are first of all metals

of transition groups (Mn, Cr, V, Ni, Cu, Pb) present in kaolins in much smaller quantities then Fe and Ti but exhibiting strong chromophorus character. Other trace elements such as e. g. Sr, Ba and Zr may influence the whiteness of kaolins particularly so after firing.

Particular attention has been given to Pb, Sr and Ba as these elements occur in increased quantities in the kaolins, 10 to 20 times larger than other trace elements (Table 2). Lead, strontium and barium show distinct tendency to concentrate in fine fractions of the kaolins which is well discernible in secondary kaolins. In the primary kaolins the distribution of the above elements into fractions is not always

TABLE 2

Lead, strontium and barium content in the Lower Silesian kaolins (in ppm)

Deposit, number of the sample, fraction in μm		Pb	Sr	Ba
Bolesławice				
1.	<2	1000	290	530
	2—5	300	60	230
2.	<2	120	67	170
	2—5	70	31	160
Wyszonowice				
1.	<2	1000	70	220
	2—5	1000	100	500
2.	<2	32	50	150
	2—5	38	42	110
Maria III				
1. industry washed sample		652	749	271
	<2	920	360	420
	2—5	200	270	300
2.	5—15	180	210	230
	15—30	39	110	200
	30—60	37	140	210
Czerwona Woda				
1.	<30	750	610	270
	30—60	100	55	-25
	<30	1000	440	280
2.	30—60	210	54	33

consequent. This pertains particularly strontium and barium as well as kaolins of low kaolinization degree, in which sometimes two maxima of concentration can be noted.

In the studies carried out so far it has been assumed that those elements occur in kaolins in adsorbed form on the surface of kaolins and other clay minerals or in form of admixtures in non decomposed minerals of parent rocks.

Recent studies have shown that the high content of Pb, Sr and Ba is associated with the occurrence in kaolins of their own minerals of the goyazite $SrAl_3(PO_4)_2(OH)_5 \cdot H_2O$ and plumbogummite $PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$ type. These minerals belong to hydrated basic aluminum phosphates rarely found in nature (aluminum can be partly substituted by iron and or strontium, barium, calcium, cerium and other divalent elements). Because of their similarity in chemical composition and structure they are treated together with alunites with which they can form solid solutions [KASZKAJ, 1970.]

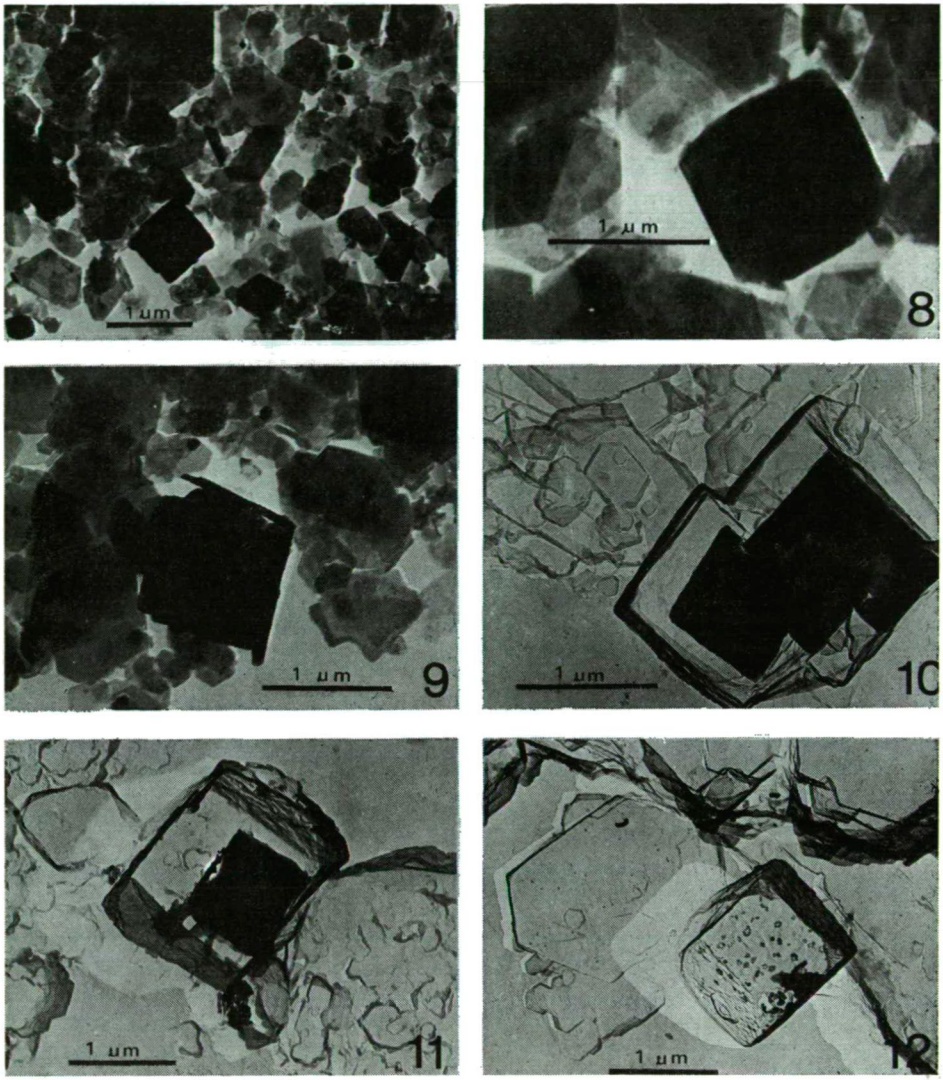

PLATE II

7. Maria III kaolin. Phosphate grains among kaolinite flakes (suspension)
8. Maria III. kaolin. Phosphate grain (suspension)
9. Maria III kaolin. Phosphate grain with attached kaolinite flakes (suspension)
10. Maria III kaolin. Phosphate grain partly etched (replica)
11. Czerwona Woda kaolin. Phosphate grain, partly etched (replica)
12. Maria III kaolin. Phosphate grain almost completely etched (replica)

Grains of phosphate minerals have been found in preparates of fine fractions in all secondary and primary kaolins. In suspension preparates they are opaque for electron beam. In secondary kaolins their sections are close to squares or rectangles sometimes

with truncated corners and are similar to anatase from which they are easily distinguishable as they are less resistant to HF (Plate II, 7—12). In the primary kaolins the phosphates are less regular and frequently form aggregates (Plate III, 13—16). The phosphates are gradually dissolved in HF which can be observed on Plate II, 10—12. Fragments preserved inside the replicas of not completely dissvoled phosphate grains allowed to obtain electroncgrams the interpretation of which proved earlier identification.

The X-ray images of those minerals are presented on *Fig. 2*. Aluminum and phosphorus are the main elements of the analysed grains. Beside them there are strontium, lead, barium, calcium, cerium, lanthanum and arsenic. Out of those elements only Sr and less abundant Ca and Ce were present in all analysed grains. Lead has been stated in several grains in variable quantities, and it should be mentioned that this element replaces strontium. In samples of high strontium content the lead lines are usually weak *(Fig. 2a)*, whereas in samples in which lead is the dominant element the strontium occur in subordinate quantities *(Fig. 2b)*. In samples is which both the strontium and lead are present in small quantities the content of cerium increases distincly *(Fig. 2c)* i. e. florencite appears — $CeAl_3(PO_4)_2(OH)_6$.

The X-ray images shown in *Fig. 2* of selected grains of phosphate minerals derived from various kaolins seem to point that we have here several mix-crystals com-

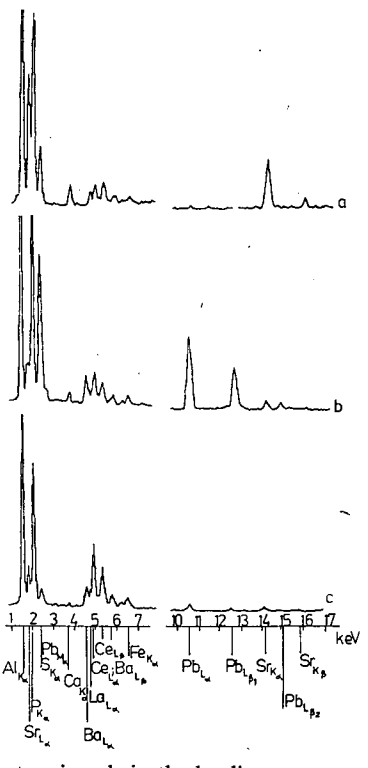

Fig. 2. X-ray images of phosphate minerals in the kaolin
a) phosphate in the Czerwona Woda kaolin (grain presented on Plate II, 11),
b) phosphate in the Maria III kaolin (grain presented on Plate II, 8),
c) phosphate in the Boleslawice kaolin (grain presented on Plate III, 13)

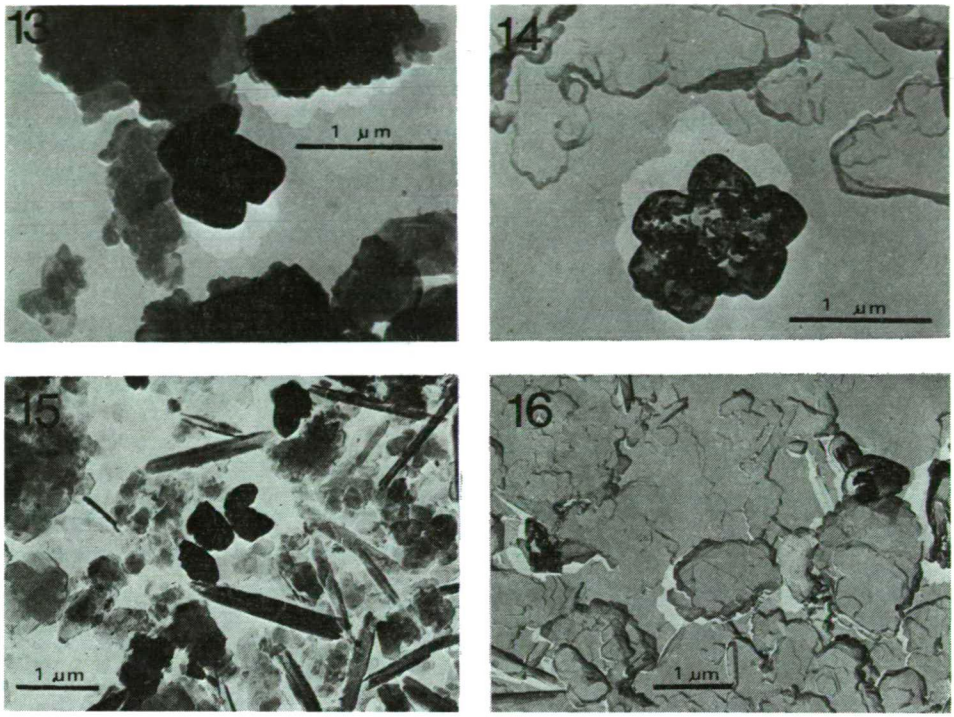

PLATE III

13. Bolesławice kaolin. Aggregate of phosphate minerals (supension)
14. Bolesławice kaolin. Aggregate of phosphate minerals (replica)
15. Wyszonowice kaolin. Kaolinite, halloysite, phosphates (suspension)
16. Wyszonowice kaolin. Kaolinite, halloysite, micas, anatase and phosphates (replica)

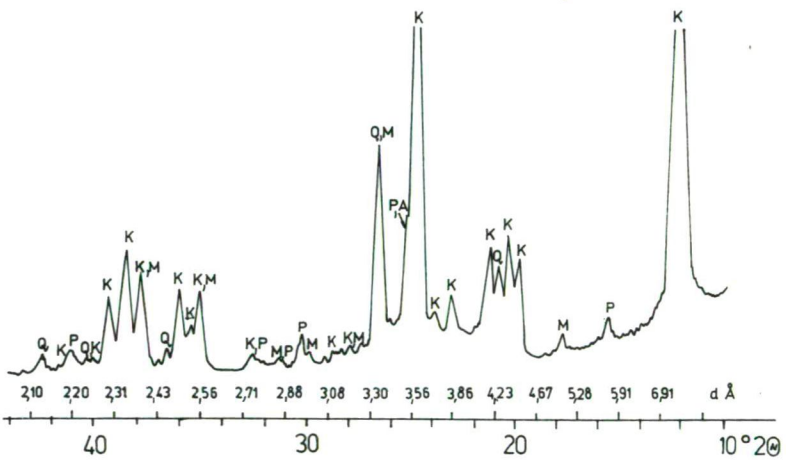

Fig. 3. X-ray diffractogram of <4 µm fraction of the Maria III kaolin
K — kaolinite, M — mica, Q — quartz. P — phosphate, A — anatase.

posed of goyazite (Sr) — plumbogummite (Pb) — florencite (Ce) — gorceixite (Ba). The lanthanid elements and cerium in particular are present in all analysed phosphates but their X-ray maxima are distinctly stronger than those of primary kaolins.

Presence of phoshates in the kaolin fraction $<4\ \mu m$ enriched in accessory minerals by means of flocculation method has been proved by X-ray analysis on the basis of diffraction lines of interlayer distance 5.72, 2.96, 2.205, 2.197 and 1.750 Å *(Fig. 3)* [SZPILA, DZIERZANOWSKI, 1977]. All the above mentioned reflections coincide with the data of minerals of the woodhousite and crandallite group [JCPDS, 1972).

The origin of the phosphate minerals in kaolins is not easy to explain. Peculiar physico-chemical conditions are necessary for their origin in which aluminum that is inert in hypergenic environment could pass into the solution and then precipitate in form of phosphates. Phosphorus and the remaining trace elements could have been present in sufficient quantities in every environment although their association with the volcanic activity cannot be excluded. Basic volcanism was intense in the area of Lower Silesia during the Tertiary, i. e. during the period in which the processes of kaolinization were intense.

Hydrophosphate of aluminum and barium — gorceixite — has been stated in kaolinite clays of the Bohemian Highland where its origin is associated with the argillitization of eruptive rocks [POVONDRA, SLANSKY. 1966]. Related to the above mentioned phosphates alunites commonly occur in products of kaolinization of eruptive rocks [GARD, 1971, MARTIN-VIVALDI, 1963]. Initial investigations carried out by the present authors prove the occurrence of phosphate minerals also in some kaolins from the Czechoslovakian and East German deposits. It can be assumed that the high Ba, Sr, Pb, Cu and P content in the Bavarian kaolins from the Hirschau-Schnaittenbach deposits found by KÖSTER [1978] is associated with the occurrence of the above phosphates.

The occurrence of Sr, Pb and Ba in form of own minerals resistant to various chemical agents explains considerable inertion of these elements in the processes of chemical bleaching of the kaolins [SZPILA, 1976a]. The find of minerals of the goyazite, plumbogummite and florencite type in the primary and secondary kaolins is of great importance in tracing the geochemical migration of these elements in the hypergenic processes. It may be assumed that under certain conditions the phosphate ions as it the case with the sulphide ions, influence the elimination of considerable quantities of Sr, Pb, Ba, Ca, Ce and other elements from the geochemical migration.

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MINERALOGICAL INVESTIGATION OF DEGRADED KAOLINITES FROM DUNÁNTÚL (TRANSDANUBIAN) AREA

G. BIDLÓ

ABSTRACT

In the Dunántúl area clay occurrences with degraded kaolinite were found. These kaolinites can be well characterised by thermoanalytical methods. In the X-ray diffraction pattern the basal reflection is absent.

In the last years a series of clay samples were investigated. The clay mineral content of them was thermoanalytically well characterized, but the basal reflections in the X-ray diffraction pattern were absent. These clay samples were mostly red-clays. This kaolinite type was also found in different types of other sedimentary rocks. In Dunántúl area there exists an older type in connection with Permian and Mesozoic and a younger type in connection with Pannonian and Pleistocene *(Fig. 1)*. The older type was investigated.

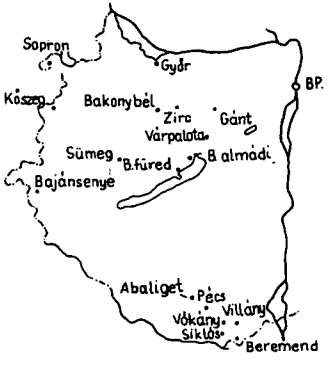

Fig. 1. Occurrences of samples investigated

The material may be characterized:

a) thermoanalytically:
1. high absorbed water content,
2. convex peaks at 300 °C in DTA curves
3. an intensive endothermic reaction at 550 °C
4. the loss of weight at 550 °C may be 8% or more,
5. a characteristic endothermic-exothermic inversion between 850 and 920° without loss of weight. *(Fig. 2)*

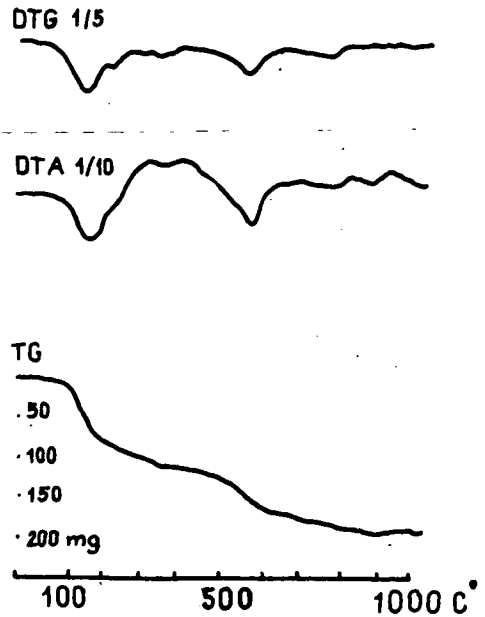

Fig. 2. Derivatographic curves of degraded kaolinite (Siklós)

b) by X-ray patterns:

1. basal reflection (0,713 nm) absent or very weak,
2. 0.448 nm reflection very strong,
3. 00l reflections weak, hk0 reflections strong. *(Fig. 3)*

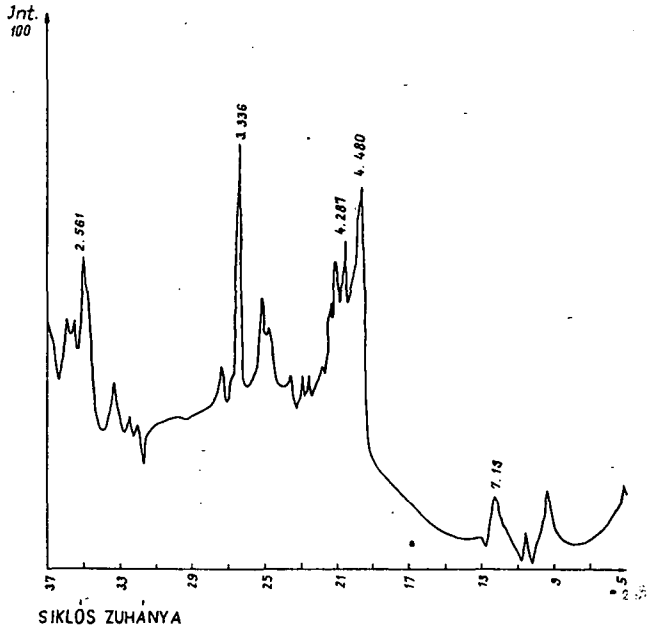

Fig. 3. X-ray pattern of degraded kaolinite (Siklós)

It was not possible to prepare pure material until now, therefore chemical composition could not be determined. Few samples of this material were investigated by electron microscopy and electron diffraction by dr. I. DÓDONY, too. The result of these investigations proved that all these samples were kaolinite.

Occurrences:

a) In connection with Mesozoic carbonate sediments:

1. In Villány Mountains (southern Hungary). The material is underlain by Mesozoic limestone and covered by loess.
2. Samples from northern Bakony Mountains are found also on Mesozoic limestones or dolomites and there they are covered by young sedimentary rocks. In the two mountains also well crystallized kaolinite can be found.

b) In connection with Permian red sandstone near to Lake Balaton:
In the northern side of Lake Balaton Permian sandstone strata are found. In the red-stone clay strata are situated between the sandstone strata. This clay has a degraded kaolinite content.

c) Other occurrences (characterized only by means of derivatograph):

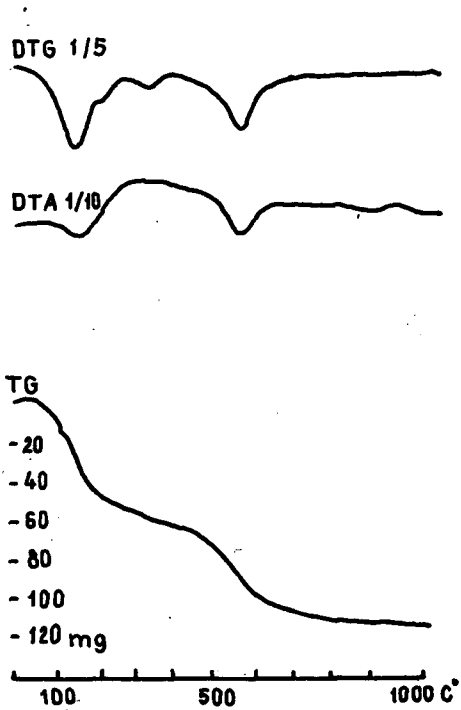

Fig. 4. Derivatographic curves of solution residue of a limestone ("marble") from Villány

Western side of Mecsek Mountains at Abaliget, on Mesozoic limestone. Red clay at Sümeg on Mesozoic limestone. The mineral components of the insoluble residue of Ladinic limestone ("marble") of Villány is similar to those of the investigat-

ed samples mentioned above. The only difference was, that in X-ray pattern a reflection at 1.001 nm was found. *(Fig. 4)*.

It was observed that these degraded kaolinite occurs in those Mesozoic areas where also Jurassic and Cretaceous rocks can be found.

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X-RAY VARIANCE METHOD TO DETERMINE THE DOMAIN SIZE AND LATTICE DISTORTION OF GROUND KAOLINITE SAMPLES

M. N. TÓTH

ABSTRACT

The variance method [WILSON, 1963] was applied to determine the changes in domain size and lattice distortion along the 001 direction in dry grinding experiments of Sedlec (Zettlitz) kaolinite samples. Very short grinding (3 min) already resulted in considerable lattice distortion, while change in domain size is of minor extent. A grinding of 30—40 min converted the medium crystallized Sedlec (Zettlitz) kaolinite into a substance which had an X-ray diffraction pattern similar to that of poorly crystallized kaolinite$_d$.

INTRODUCTION

In an earlier paper I dealt with the changes in the crystallinity parameters of kaolinite on a sample series of artificially destructed structure (by means of dry grinding). I proposed to introduce a complex crystallinity index to characterize the state of crystallinity. This index proved to be appropriate to trace the changes due to the effect of grinding which affect the X-ray diffractogram pattern.

The complex crystallinity index (CCI) turned out to be very useful also for the comparison of natural state samples. However, it provided no numerical information on two very important parameters, grain size and lattice distortion. The components due to domain size and lattice distortion could not be distinguished in the distortion of the diffraction profile. (The effects of deformation and domain size appear superimposed).

It was necessary to undertake a more thorough analysis of the 001 reflections, in addition to the determination of half width, which does not provide sufficient information. In many cases, when kaolinites of rock samples are studied, as a consequence of coincidences only the 001 reflexions can be well measured, particularly well the 001 which is the strongest peak of kaolinite. In the experiments reported now, series of artificially destructed kaolinites was examined. A more exact mathematical procedure was applied than in the previous experiments, in order to complete the results obtained at the application of the CCI with the changes in determination of domain size and lattice distortion.

The variance method [WILSON, 1962, 1963] was used to calculate the coherently dispersed domain size resulted during grinding as well as the deformation of the lattice in the direction 001.

SAMPLE PREPARATION AND X-RAY TECHNIQUES

An amount of 2g of Sedlec (Zettlitz) kaolinite was submitted to dry grinding in a grinding mill of type Fritsch Pulverisette—2, for 3, 5, 10, 15, 20, 30 and 40 minutes. The powders obtained were kept in an exsiccator for 24 hours.

The X-ray tests were performed by means of a Philips X-ray diffractometer, as follows: radiation: CuK_α, monochromator: graphite, goniometer speed: 1/2°/min, divergency and detector slits: 1°, proportional counter, time constant: 2, recording speed: 1600 mm/h.

The line profiles were measured by 0,05° 2Θ steps intervals, usually in the range of 11,00° 2Θ—13,45° 2Θ.

MATHEMATICS USED

The variance, i. e. the reduced second moment of the line profile, was established in order to study the line widening of the 001 reflexions, to distinguish the effect of domain size and lattice distortion, making use of the results by WILSON [1962, 1963] and MITRA [1969].

The reduced second moment of the intensity function is, by definition

$$W(2\Theta) = \frac{\int (2\Theta - \langle 2\Theta \rangle)^2 \, I\,(2\Theta)\, d\,(2\Theta)}{\int I\,(2\Theta)\, d\,(2\Theta)}$$

where $\langle 2\Theta \rangle$ is the centroid of the line.

The variances being additive, the resulting variance of one line profile is

$$W(2\Theta) = W_o + W^p + W^d$$

where W_o, W^p, W^d are the variance values due to instrumental error, domain size and lattice distortion, respectively.

If the tails of the line profiles show the Cauchy distribution, i. e. they are approaching asymptotically the background, then variance is a linear function of the chosen angle range [WILSON, 1963].

The domain size and lattice distortion can be deduced from the ordinate incept and slope of the following equation [WILSON, 1963]

$$W\,(2\Theta) \cos \Theta \,/\, \lambda\,(\Delta 2\Theta) = {}^1/\pi^2 p + 4 \sin \Theta \operatorname{tg} \Theta \, \langle \varepsilon^2 \rangle \,/\, \lambda\,(\Delta 2\Theta)$$

where p is the effective domain size, $\sqrt{\langle \varepsilon^2 \rangle}$ is the expected value of the lattice distortion.

RESULTS

Variance, centroid, 001 directional domain size and lattice distortion were determined by using a program written for EMG—666 type computer.

Variance is very sensitive of the background. This made indispensable certain background corrections. *Fig. 1* shows the variance as a function of range. It is to be seen that the variance is linear in function of the chosen angle range.

Table 1. contains the centroid and variance value. The lowest row represents the data of Cserszegtomaj kaolinite (Hungary) which is disordered along axis *b*.

The centroid values also have been determined to calculate the variance. As a result of grinding, the centroid values shifted towards smaller 2Θ angles. This reflects a lattice dilatation according to axis *c*. This is in harmony with the statement made by FIEDLER and STEINICKE [1967], namely, that the *d* value of the 001 reflexion of poorly crystallized kaolinite is higher. Even 3 minute of grinding had a considerable effect on the centroid value.

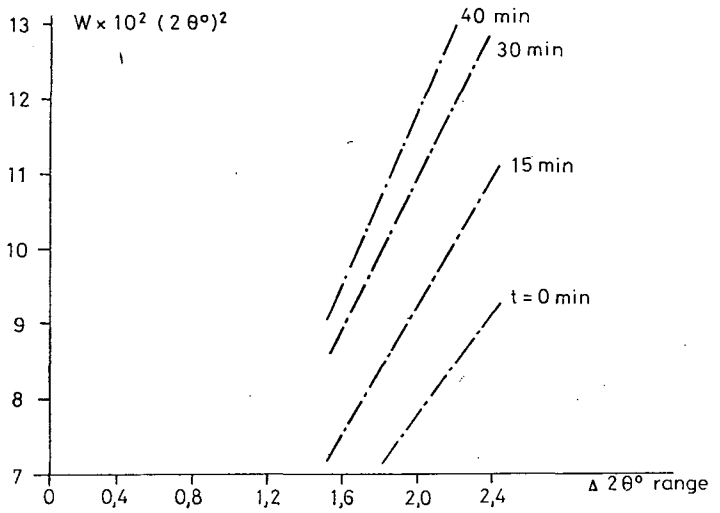

Fig. 1. Variance versus integration range

As mentioned before, the change in the half width of the 001 base reflexion is a result of line widening due to domain size and lattice distortion. In the experiment, the half width value of the 001 basal reflexion changed from 0,39° 2Θ to 0,42° 2Θ *(Fig. 2)*. Accordingly they belong to the range of poorly crystallized kaolinite, in harmony with the results published by BRINDLEY and KURTOSSY [1961], i. e. 0,3—0,4° 2Θ.

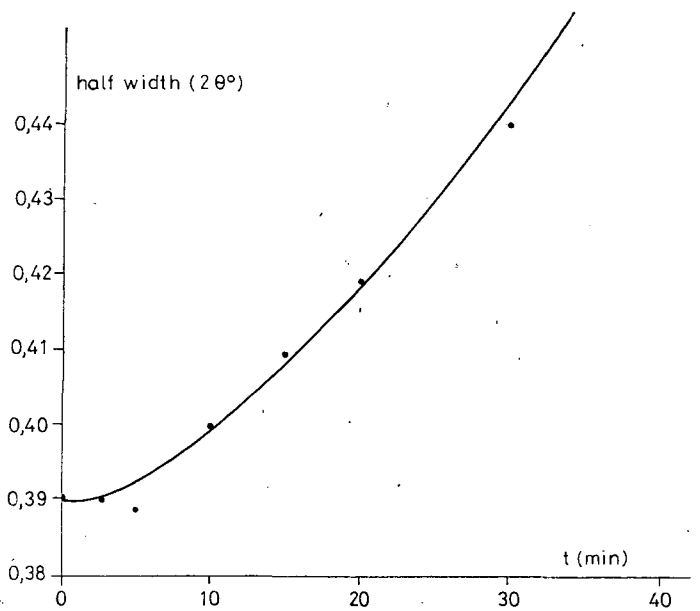

Fig. 2. The half width of 001 reflexion as a function of grinding time

TABLE 1

Variance analysis data

Grinding time (min)	Centroid ($2\Theta°$)	Variance ($2\Theta°$)	Range ($2°\Theta$)
0	12,2691	0,09505	2,45
3	12,2264	0,09662	2,45
5	12,2223	0,10003	2,45
10	12,1942	0,10867	2,40
15	12,1869	0,11335	2,40
20	12,1610	0,12970	2,40
30	12,1493	0,13525	2,40
40	12,1142	0,12952	2,40
Cserszegtomaj	12,2134	0,12775	2,40

The changes in lattice distortion domain size provoked by grinding are illustrated in Table 2. Deformation changes at a higher rate in the early phase of grinding. About 30—40 minutes of grinding brought the deformation values of the medium crystallized Sedlec (Zettlitz) kaolinite near to that of Cserszegtomaj kaolinite$_d$. (Table 2 and *Fig. 3*). Similar results have been obtained in the case of the CCI, too.

Domain size change is less important in case of short time grinding: in 30—40 minutes, however, the quasi-minimum values are obtained. It is very likely that

TABLE 2

Data of domain size and lattice distortion

Grinding time (min)	Domain size (Å)	Lattice distortion $\times 10^3$
0	120	6,34
3	122	6,68
5	117	7,10
10	110	7,63
15	104	8,22
20	88	9,01
30	91	10,34
40	87	11,30
Cserszegtomaj	100	12,90

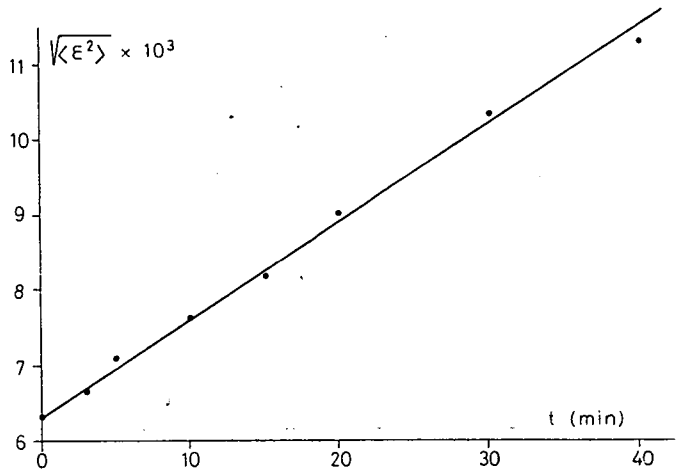

Fig. 3. Change of lattice distortion versus grinding time

amorphization begins in this phase *(Fig. 4)*. The trends of changes in domain size and lattice distortion show a fairly good agreement with the statement of KRANZE [1975] who pointed out that at the beginning of grinding lattice distortion is the more important change.

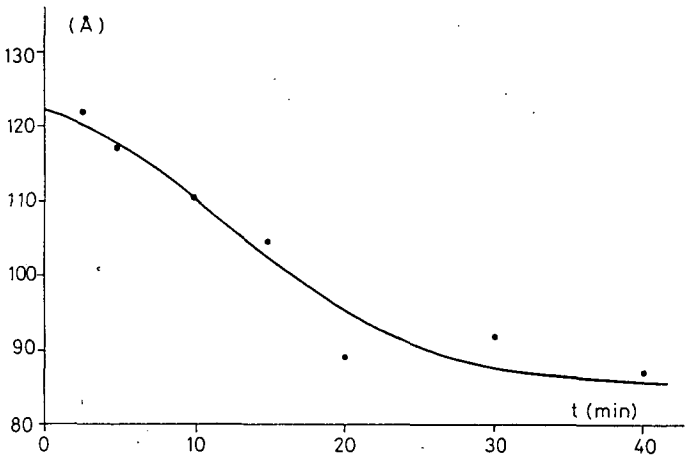

Fig. 4. Change of domain size versus grinding time

The present results emphasized once more the bearing of the proper choice of grinding time. The procedure of grinding affects two parameters, domain size and lattice distortion, which are also of genetical importance.

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MECHANO-CHEMICAL ACTIVATION OF KAOLIN MINERALS

ZOLTÁN JUHÁSZ

ABSTRACT

Tests have been made to study processes during the intensive grinding (supergrinding) as mechanical activation of kaolins. Activation was made by dry grinding for different times in a vibrating mill. Conclusions:

1. Change of the inner morphology of kaolin powders is due to three partial processes: disintegration, aggregation and agglomeration. The first one prevails for a short activation time, the latter two being overwhelming in prolonged activation. Therefore the grade of dispersity initially grows to decrease after prolonged grinding. In this latter case, compacted aggregates result, inacessible to soaking in water, even if a peptizer is added. Also plasticity of the kaolin-water system decreases.
2. Supergrinding also affects the mutual adhesion, adsorption properties and action exchange capacity of kaolin particles as well as the acid solubility of kaolins very much. Test data hint to surface activation. At the same time, surface active centres will be covered by neighbouring particles ("overlapping effect").
3. Supergrinding causes amorphization of the crystal structure, beside appearance of fireclay structure. Amorphization is bound to a critical crystallite size, and has different rates along each crystallographic direction.
4. Destruction of the crystal structure of kaolinite is concomitant to the release of water of structural OH groups followed by incorporation of water into a gel structure. Xerogel when heated yields stable phases at the same high temperature as the original kaolinite. The high-temperature sintering process is, however, somewhat different in the two materials.
5. Mechano-chemical processes are somewhat accessible to artificial influencing by preliminary ion exchange.

INTRODUCTION

"Mechanical activation" is understood as to increase the free energy of solid systems by mechanical effects, changing the inner morphology of solids e. g. reducing the particle size of dispersed systems, or increasing the specific surface by deformation. But the crystal structure may also be modified, e. g. deformed, the number of lattice defects may increase, even degree of crystallinity may decrease. This latter case of changes affecting chemical bonds is referred to as "mechano-chemical activation" often accompanied by polymorphic transformations and chemical reactions [JUHÁSZ, 1974].

The simplest way of mechanical activation is grinding. Mechanical activation is conditioned by an equipment providing very intensive grinding e. g. in vibrating or ball mills for a very long time, referred to as "supergrinding".

In the following, morphological and structural changes in kaolin supergrinding will be considered. Research has been governed partly by practical, and partly by theoretical aspects. Practical aspects included determination of quality changes in kaolin grinding, and of the effect of kaolin sample preparations (pulverization) on

material testing results; theoretical research concerned causes of these phenomena. The recognized processes may be assumed to be of importance for the development and further transformations of natural kaolins, in conformity with the given geological conditions and outer mechanical effects.

SURVEY OF PUBLICATIONS

The phenomenon of kaolin crystallinity loss after prolonged grinding has long been known. KELLEY and JENNEY [1936] reported transitory widening of X-ray lines, followed by complete decomposition of the crystal structure after prolonged grinding, a statement confirmed by several subsequent investigations.

Owing to the fact that grinding is of high importance for the preparation technology of kaolin minerals, and application in ceramics, many research has obviously been spent on morphological and structural changes due to wet and dry grinding [KÖHLER, 1960; WIEGMANN, 1957; SHAW 1942; PERKINS, 1948; HAASE, 1959]. According to these investigations structural transformations are moderate or missing while particle size reduction is important upon wet grinding of kaolins. On the other hand, in dry grinding, crystal structure is destroyed, amorphization is, however, accompanied by a slight particle size reduction. In this latter case, prolonged grinding may even be accompanied by a decrease of the specific surface [AKAMATU, 1965; JUHÁSZ, 1969]. Aggregates responsible for the decrease of the specific sufrace are assumed to have a structure like a Hofmann-type house of cards [KÖHLER, 1960].

Destruction of the kaolin structure in grindig has been experimentally demonstrated by thermal analysis, X-radiography and IR absorption methods [HLAVAY, 1976]. As a rule a disordered crystal structure arises first, passing into a fully amorphous one after prolonged grinding. SCHRADER *et al.* [1970] comprehensively investigated mechano-chemical transformations of the kaolin structure. Increasing the grinding time, the particle size decreased (slightly) along the *c* axis, but rather rapidly and significantly did so along the *b* axis, causing kaolin to loose its lamellar habit. At the same time crystal structure was deformed mainly along the *c* axis, being more resistant along the *b* axis. In an intermediate phase of transformation kaolinite passes into a fireclay structure.

Several authors have observed appearance of fireclay structure in grinding [LAWS, 1946; WIEGMANN, 1957; JUHÁSZ, 1969].

LEHMANN [1955] observed a DTA-curve like that of illite, MILLER [1970] reported on a phenomenon of fast prototropy.

Also modification of cation exchange capacity and adsorptivity upon grinding of kaolin may be explained partly by the increase of specific surface, and partly by changes of the crystal structure. Cation exchange capacity is normally increasing or follows a maximum curve *vs.* grinding time [GREGG, 1954; KÖHLER, 1960; SANYAL, 1961; BARTHOLOMÄ, 1960; JUHÁSZ, 1969]. Increase of water adsorptivity and of adsorption energy refers to the increase of surface active energy of kaolin crystals [HAASE, 1959], and so does the increase of the activity of kaolin catalysts [AKAMATU, 1965] and that of the methylene blue adsorptivity [BARTHOLOMÄ, 1960].

The combined effect of crystal structure amorphization and of the specific surface increase may be responsible for the increase of kaolin solubility after grinding [OCEPEK, 1966]. BARTHOLOMÄ and SCHWIETE [1960] stated the total Al, Fe, Na, K and Ca to be dissoluble from suficiently activated kaolin using dilute hydrochlorid acid, the residual being practically pure silica gel. According to GREGG *et al.* [1954], solubility monotonously increases with the grinding time, while the specific surface

varies according to a maximum curve, ascribing the increase of solubility not only to the increase of active surface but also to the decrease of crystal stability.

In general, wet grinding has been observed to improve, and dry grinding to impair the plastic properties of kaolin [KÖHLER, 1960], although some improvement is possible in the initial stage of dry grinding. This is why wet grinding is preferred to dry one for ceramic kaolin.

No uniform views have developed concerning firing properties after grinding. Sintering seems to be primarily affected by the particle size rather than the degree of amorphization [HILLER, 1968]. LÖCSEI [1970] ground kaolinite with 13% of AlF_3 and then heated it. More mullite has developed in heating, at a lower temperature (650 °C). Grinding is likely to favour metakaolin → spinell transformation, just as high static pressure [BLAIR, 1972].

After mechanical activation, reactivity of kaolin to CaO was found to increase greatly. MEHTA [1971] made cement from superground kaolin — mixed with lime — without thermal energy utilization. Direct chemical reactions were found to occur during the combined grinding of kaolin and CaO.

RESEARCH METHOD

Our tests involved kaolin samples of different origin, with symbols, oxide and mineral compositions compiled in Table 1. Mechanical activation of kaolin samples pre-ground to below 60 μm was made in a laboratory vibrating mill type KEFAMA containing 2-litre grinding pans. Materials with different activities were produced by varying the grinding time (vibration amplitude of the mill was 2 mm, at a frequency of 1300/min; charge: 60 g of sample, and 2100 g of steel balls ∅ 2 to 10 mm).

Activated materials have been examined from the following aspects:

— powder morphology;
— particle surface texture;
— crystal structure;
— aqueous suspension properties and
— heating behaviour.

TABLE 1

Oxide and mineral composition of the samples

Symbols: Occurrences:	SzK Szegi	SzF Szegi	SK Sárisáp	HK Mád-Hercegköves	ZK Sedlec (Zettlitz)
SiO_2	46,1%	49,0%	60,5%	47,8%	45,6%
Al_2O_3	34,2	31,6	27,5	37,3	37,0
Fe_2O_3	3,24	3,24	1,12	0,31	1,10
CaO	0,65	0,70	0,66	0,10	1,10
MgO	0,68	0,65	0,26	0,05	0,10
K_2O	0,10	0,12	0,61	0,01	0,78
Na_2O_3	0,07	0,10	0,10	0,01	0,30
H_2O	14,85	13,97	8,75	13,91	14,5
Kaolinite minerals:	92 (kaolinite)	95 (fireclay)	63 (kaolinite)	92 (dickite)	87 (kaolinite)
Illite	3	—	9	—	7
Montmorillonite:	—	—	—	4	—
Quartz:	4	5	26	4	6

From the aspect of inner morphology, in the aggregation structure of a powder — e. g. of kaolin — three parts may be distinguished:

1. Solid skeleton, bulk of primary kaolin crystal particles as an independent phase (solid part of the dispersed system).
2. Pore system: primary particles normally join secondary particles accommodating open and closed pores, capillaries, voids, possibly cracks composing a pore system dispersed throughout the aggregation.
3. Void system: coherent particle interstices in the loose powder aggregation.

Accordingly, as a first approximation, inner morphology of powders may be described in three different ways:

Volume percentages

In a bulk of 1 ml, volume ratios of solids, pore system and void system are compactness ξ, porosity ε and voids ratio $\varkappa$, respectively:

$$\xi = \frac{\varrho_H}{\varrho}; \qquad \varepsilon = \frac{\varrho_H}{\varrho_T} - \frac{\varrho_H}{\varrho}; \qquad \varkappa = 1 - \frac{\varrho_H}{\varrho_T}$$

(ϱ=density, ϱ_T particle density, and ϱ_H=aggregation density).

Accordingly, morphological state can be represented in the state diagram of compactness, porosity, voids ratio [in the TPH system; JUHÁSZ, 1978].

Particle porosity (in a theoretically voidless system):

$$\varepsilon_0 = 1 - \frac{\varrho_T}{\varrho}$$

Specific surface

Specific surface reduced to 1 g of primary and secondary particles in the powder:

$$S_V = \frac{a_P + a_H}{m}; \qquad s = \frac{a_H}{m}$$

a_P and a_H being interstitial surfaces between pores and primary particles, and those between voids and secondary particles, resp., m is mass of the sample. The value of S_V has been determined from the BET relationship applied on vapour adsorption isotherms, those of ε_0 and s according to our earlier published method based on the measurement of powder permeability [JUHÁSZ, 1978]. S_V is the "dispersity degree", and s the "grinding fineness" of the system.

Granulation

Grain size curves (of aqueous systems) will be presented later. Particle shape has been tested under a scanning electron microscope.

— · —

Test data of two different kaolin samples have been plotted in *Figs 1* and *2*, exhibiting two distinct periods of activation:

1. The initial period (about 0 to 12 h of grinding time) is mainly characterized by the increase of the dispersity degree — i. e., fracture, disintegration of primary particles. Both samples being *a priory* very fine, washed kaolins, the grinding fineness

hardly changed in this period of grinding. This is, however, no general phenomenon, since in the initial period the grinding fineness mostly markedly grows for most silicate minerals. This period is generally characterized by mechanical dispersion.

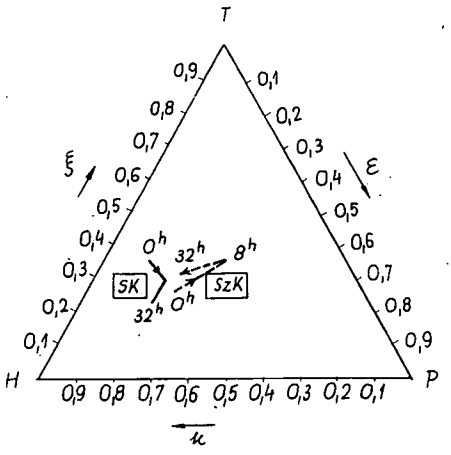

Fig. 1. Morphological changes in powders of kaolins from Sárisáp (SK) and Szegi (SzK) plotted in the morphological diagram of state compactness — porosity — voids ratio (TPH system).

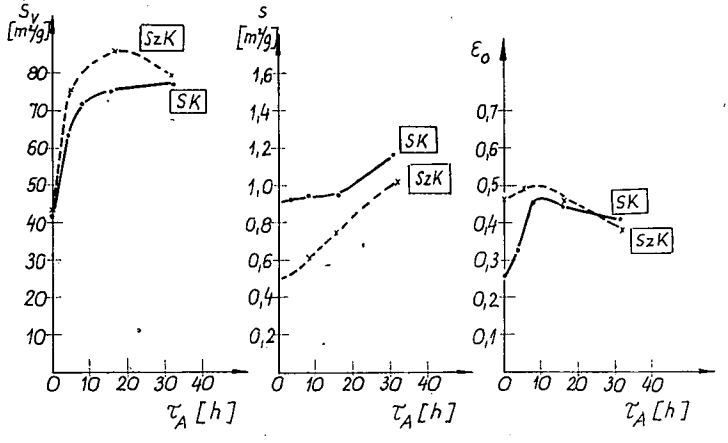

Fig. 2. Dispersity degree S_V, grinding fineness s and particle porosity ε_0 *vs.* grinding time τ_A

2. Electron photomicrographs made in the second period (after 12 h) show marked aggregation of primary particles *(Fig. 3)*. Mechanical effect during grinding causes aggregate compaction (decreasing ε_0), even some pores close to become inaccessible to vapour molecules. Thereby also the specific surface S_v calculated from the vapour adsorption capacity lessens. Compact secondary particles are prone to breaking with increasing grinding time, further increasing the grinding fineness.

Thus already the powder morphology diagrams point to several partial processes in the material during kaolin activation. The following ones are of importance from morphological aspects:

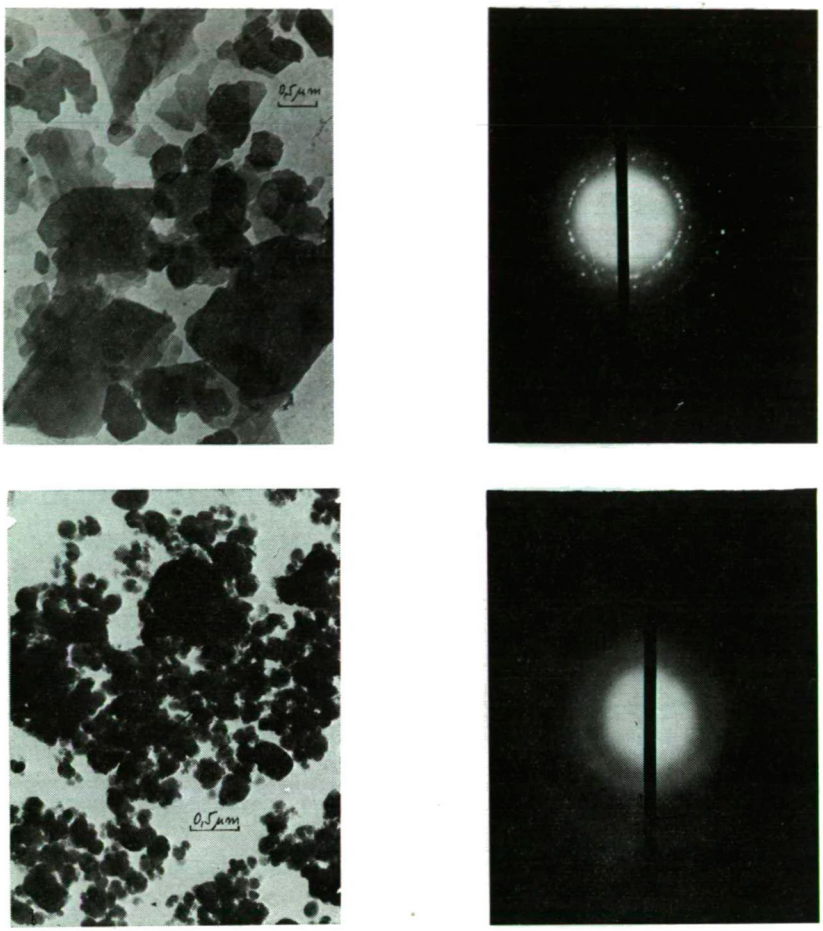

Fig. 3. Electron photomicrographs (left side) and electron diffractogram (right side) of kaolin (upper) and of kaolin-agglomerat (lower).

— Disintegration: breaking of primary and secondary particles into lesser particles. Nevertheless, partial processes of disintegration of primary and secondary particles may be independent of each other, e. g. the grinding fineness does not absolutely follow variations of the kaolinite dispersity degree.
— Aggregation: arise of secondary particles due to the interparticle adhesion. In the initial grinding period S_v increases while s remains contant indicating to a grinding equilibrium when the broken particles — as soon as arisen — aggregate to secondary ones. In grinding equilibrium disintegration and aggregation are of equal rate.
— Agglomeration: Aggregate compaction due to the effect of high surface forces, a process accompanied by fundamental changes of kaolin properties. Let us remind that the following partial processes of activation in a vibrating mill may be considered kaolins but also at other minerals: (1) initial increase

of the degree of dispersity of materials, (2) aggregate formation, (3) compaction (agglomeration) and (4) fracture (dispersion) of aggregates at a sufficient degree of compactness. All these partial processes of activation are discernible by electron microscopy.

PARTICLE SURFACE CHANGES

The concept of surface boundary layer is not the same as that of the geometrical surface. Namely an interstitial boundary layer involves the contacting surfaces of both phases, thus, in our case, atoms, ions and molecules of both the kaolin, the medium (e. g. air) and of the adsorbed „foreign" matter.

Structure of the surface boundary layer has been concluded from the following considerations:

1. Morphological stability of the powder voids system may be expressed by the specific energy of compaction, i. e. the external work spent to the compaction of the grist until its voids system completely disappears. It has been determined from step by step compaction and measurement of permeability, by graphic extrapolation. Morphological stability of the powder primarily depends on the adhesion forces between adjacent particles of the voids system.

2. The value of silicate surface polarity has been derived from the water adsorption potential ψ_V calculated from vapour adsorption isotherms, ψ_V is the energy released by 1 m² surface adsorbing water up to saturation. Its value has been calculated from vapour adsorption potential diagrams.

3. The cation exchange capacity (T value) has been determined by the modified Mehlich method. The cation exchange value has been reduced to 1 m² surface:

$$T' = \frac{T}{S_V} \qquad [\text{mge/m}^2]$$

4. Water percentage w_g% unevaporable in air at a relative humidity vapour pressure $p_r = 0{,}01$ and 23 °C but released at 380 °C has been determined as percentage of gel water and surface water with high bond energy, reduced to 1 m² of kaolin surface:

$$\alpha_V = \frac{W_g}{1800 \cdot S_V} \times 10^6 \qquad [\mu\text{m/m}^2]$$

5. Aluminum percentages dissolved from the kaolins after 2 h of boiling in 0,1 n HCl have been determined and related to the initial (total) Al in the kaolin.

Solubility for 1 m² surface:

$$l' = \frac{\text{Al}_{\text{dissolved}}}{\text{Al}_{\text{total}}\, S_v} \qquad [\text{g/m}^2]$$

Test results have been plotted in *Figs 4* and *5*. The following conclusions should be pointed out:

1. In the initial period of grinding, interstitial properties of the kaolin are hardly changing. In this period — called the range of mechanical dispersion — surface properties are mainly affected by increase of the specific surface of the system and, consequently, by increase of values characterizing the surface texture, reduced to 1 m² area.

2. In the second period of grinding (in case of our examples, beyond 4 to 8 h of grinding) appearance of high surface-active forces may be concluded on (range of "surface activation"). These forces are likely arising from chemical bonds disrupted in connection with the fracture of kaolinite crystals and getting to the new fracture

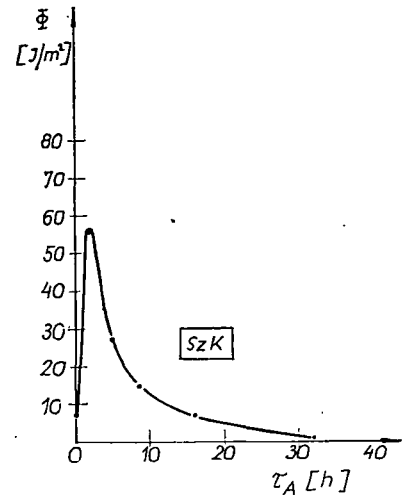

Fig. 4. Specific compaction energy Φ of powders *vs.* activation time τ_A

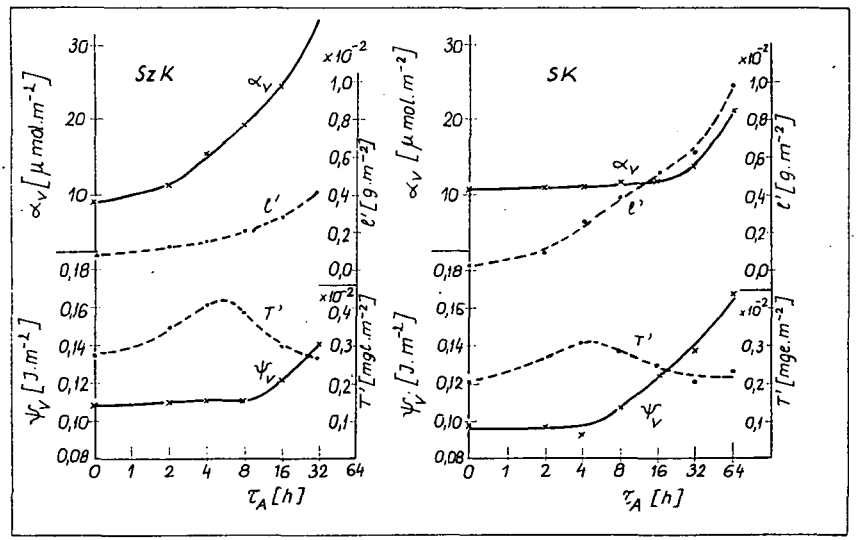

Fig. 5. Diagrams of surface texture changes

surfaces, resulting in important changes of the kaolin surface porperties. They cause e. g. the increase of inter-particle adhesion i. e. morphological stability Φ of the powder, and enhance compaction inside the secondary particles (see the variation of ε_0).

3. Surface activation and aggregation result in the variation of cation exchange capacity according to a maximum curve. Typically, however, not only the (total) T value but also the cation exchange capacity T' related to unit area do the same. Namely, although the density of ion exchange sites initially increases on the new fracture surfaces, in a longer grinding accompanied by aggregation, part of the kaolin ion exchange centres are overlapped by neighbouring particles (apparent decrease of the surface density of ion exchange sites) to become inaccessible to exchangeable ions. This phenomenon called "overlapping effect" also appears in other silicate minerals and results, in final account, in inactivation of the surface to certain reactions e. g. ion exchange reaction. The overlapping effect is also responsible for the decrease of interparticle adhesion Φ after prolonged grinding.

CHANGES IN CRYSTAL STRUCTURE

Kaolin samples ground in a vibrating mill for different periods showed gradual transformation of crystal structure in the powder.

X-ray tests

The phenomenon will be illustrated on two different kaolins, the well crystallized kaolin of Sedlec (Zettlitz), and the *a priori* fireclay type kaolin of Szegi. *(Fig. 6)* X-ray diffraction patterns clearly show gradual loss of reflection intensity and appearance of an intermediate fireclay structure parallel to the degradation of the well-crystallized kaolin structure. After prolonged grinding, both kaolins transformed to X-ray amorphous materials, with practically identical diffraction patterns. From diffraction maxima, crystallite sizes A, lattice distortion $\frac{\Delta\alpha}{\alpha_a}$ as well as the degree of crystallinity K parallel and normal to the plane of kaolinite lamellae have been calculated *(Fig. 7)*.

Conclusions:

1. In general, crystallite sizes decreased significantly, depending on the grinding time, both normal (along the c axis) and parallel (along the b axis) to the crystal lamellae. Thus, crystallites fractured during activation. Again, the process has been observed to be speedier along the c axis than along the b axis thus, the shape of crystallites gradually changed from the anisometric, (lamellar) to the isometric one, upon adequate grinding time.

2. The lattice distortion $\frac{\Delta\alpha}{\alpha_a}$ — average deviation from the ideal lattice spacing — usually monotonously increases with the activation time.

The lattice distortion process is, however, speedier along the c axis than along the b axis (shift dislocations between and inside crystal layers). Appearance of the fireclay structure is concomitant of the disorder along the b axis.

3. Also degree of crystallinity K — referred to the initial condition as 100% — abruptly decreased with increasing grinding time, but the crystalline order in the double layers got damaged more and faster along the c axis than along the nearly normal b axis.

Thermal tests

Grinding modifies also DTA curves of kaolin as shown in *Figs* 8 to *10*. Peak and valley temperatures ΔT' of an endothermic reaction at about 580 °C generally decrease

with increasing grinding time as shown by DTA curves of a very well crystallized kaolin (containing kaolinite and dickite), as well as by curves of medium-, and poorly-crystallized kaolins. A new reaction appears instead, at a temperature of about 150

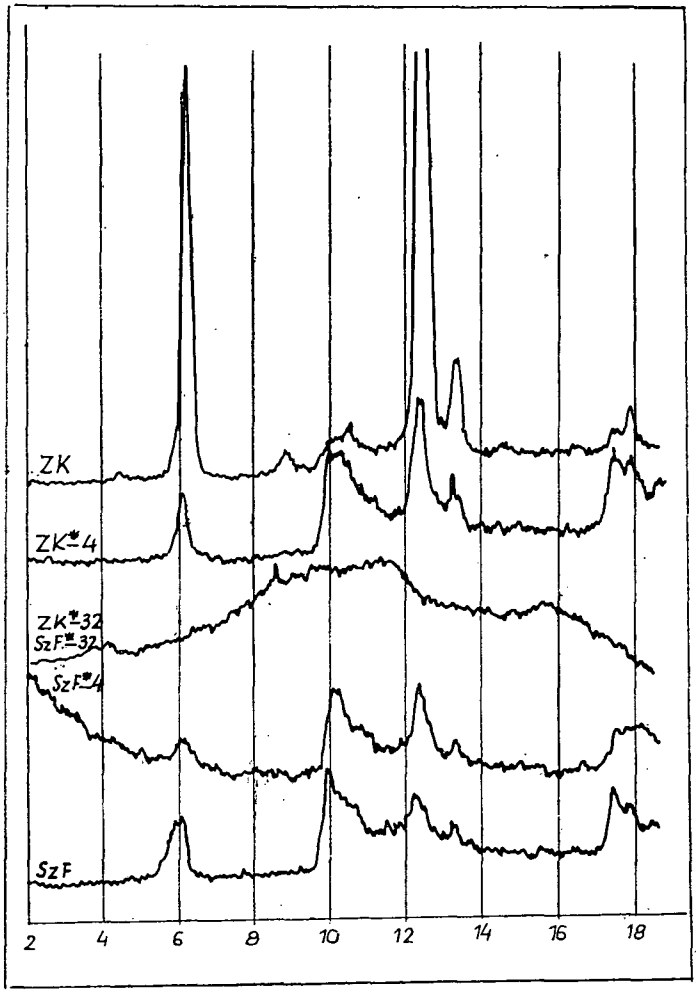

Fig. 6. X-ray diffractometric curves of kaolin from Sedlec (Zettlitz) and of fireclay from Szegi in original condition and after activation of 4 h and 32 h (activated samples marked by *

to 200 °C. Valley depth (and area) of this latter reaction varies as a function of the activation time according to a maximum curve *(Fig. 11)*.

"Structural water" calculated from TG curves — thus, percentage w_{OH} and activation energy E_{OH} of water leaving at 500 to 700 °C varied *vs.* activation time as shown in *Fig. 12*. Mainly upon prolonged grinding (supergrinding), mechano-chemical activation seems to cause OH groups to leave the kaolin structure, just as kaolin heated above 575 °C transformed to metakaolin. At the same time, kaolin is also

amorphized in supergrinding. (Amorphization R_{Ka} has been characterized by the mean line intensity $\bar{I}$ of Debye-Scherrer patterns:

$$R_{Ka} = 100 - \frac{\bar{I}}{\bar{I}_o}$$

$\bar{I}_o$ being mean line intensity of the initial sample). This mechano-chemical decomposition of the kaolin structure reminds of the (thermal) reaction of metakaolin formation, with two differences:

— At first, activation energy of water release is different, Namely, transforming a kaolinite crystal partially into metakaolin e. g. by removing only part of the OH groups (e. g. by shorter or longer, continuous heating), upon a second heating,

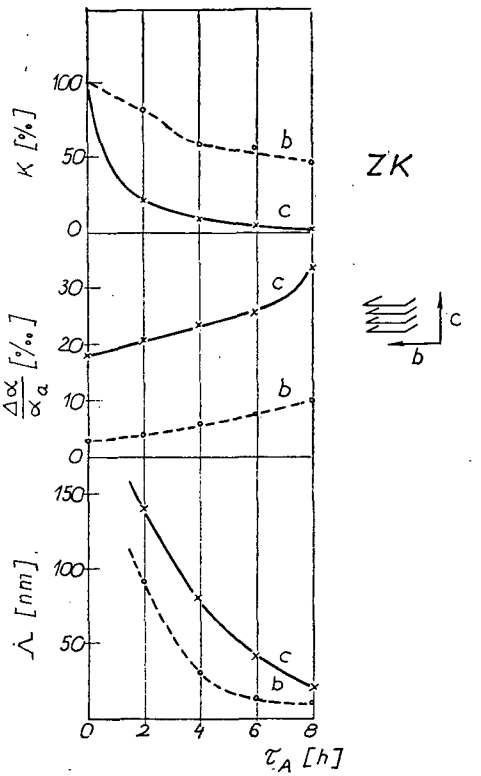

Fig. 7. Variation of crystallite size Λ, lattice distortion $\frac{\Delta\alpha}{\alpha_a}$ and degree of crystallinity K of kaolin from Sedlec (Zettlitz) along crystallographic axes *vs.* grinding time τ_A

activation on energy of water representing the rest of the OH groups in higher than, or at least the same as (but absolutely not lower than), that of the water removed earlier. On the other hand, as seen in *Fig. 12*, activation energy of residual structural water leaving the crystal structure damaged by mechanical effects is markedly reduced, indicating the decrease of the bond energy of these OH groups.

— Secondly, while metakaolin formation is accompanied by the formation of anhydrous amorphous oxides, in mechano-chemical activation, most of the water

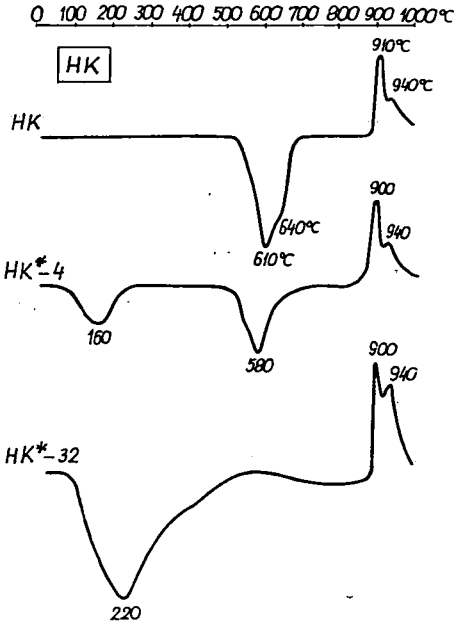

Fig. 8. DTA curves of kaolin from Hercegköves (HK)

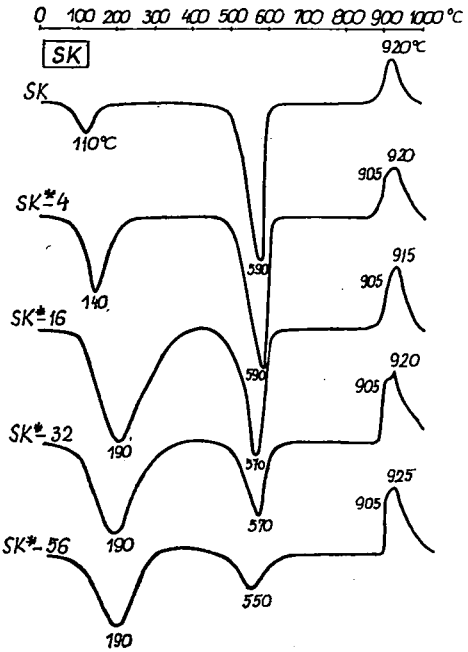

Fig. 9. DTA curves of kaolin from Sárisáp (SK)

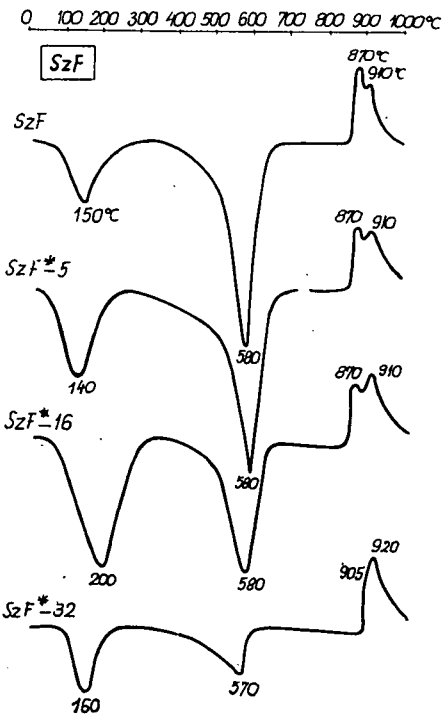

Fig. 10. DTA curves of kaolin from Szegi (SzF)

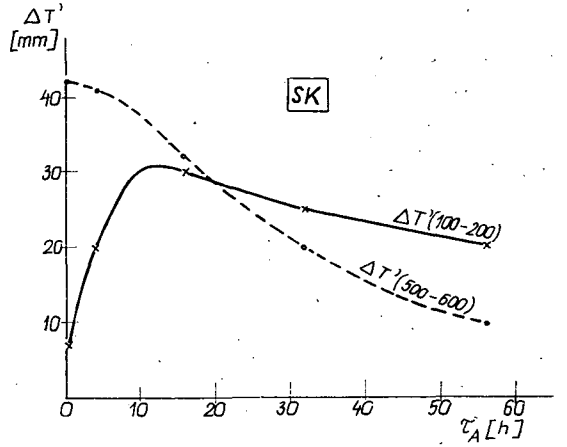

Fig. 11. First (100 to 200 °C) and second (500 to 600 °C) valley depths $\Delta T'$ of DTA curves *vs.* activation time

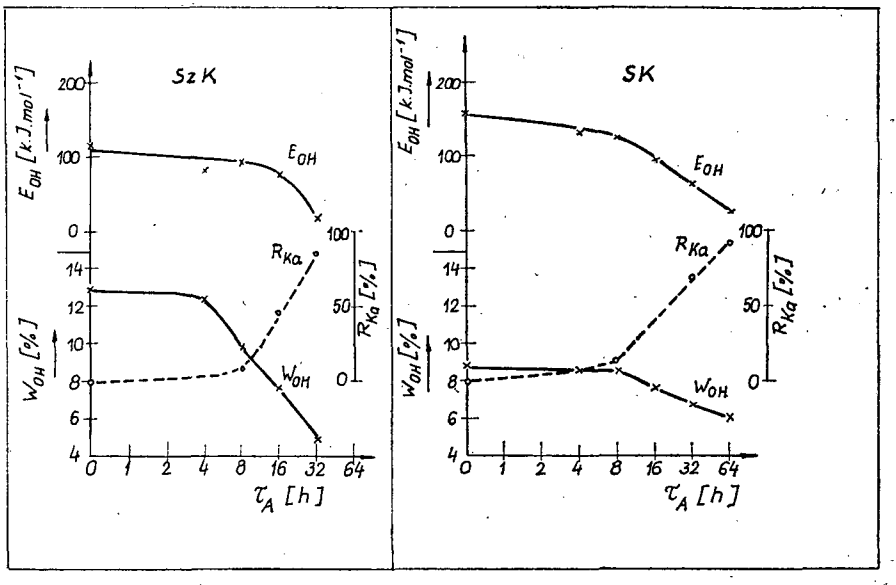

Fig. 12. Kinetic curves of the crystal structure variations of kaolins from Szegi SzF and Sárisáp SK (w_{OH} = percentage of structural water; E_{OH} = activation energy of release of structural water, R_{Ka} amorphization of the kaolinite lattice)

leaving the crystal structure is rather strongly bound by the residual amorphous silicon and aluminium oxides as gel water. Presence of this gel water appears from endothermic maxima of DTA curves at 100 to 400 °C. Upon prolonged grinding, part of the gel water is removed.

Thus, mechano-chemical reaction of kaolinite is not identical to its thermo-chemical reaction (during heating). Thermal reaction is formulated as:

$$[Si_2O_5(OH)_4Al_2]_{cryst} \rightarrow 2\,[SiO_2 \cdot Al_2O_3]_{amorphous} + 2\,H_2O_{gas}$$

There are three steps of the mechano-chemical reaction such as

$$\text{I. } [Si_2O_5(OH)_4Al_2]_{kaolinite} \rightarrow [Si_2O_5(OH)_4Al_2]_{fireclay}$$

$$\text{II. } [Si_2O_5(OH)_4Al_2]_{fireclay} \rightarrow 2\,[SiO_2 \cdot Al_2O_3 \cdot 2\,H_2O]_{amorphous}$$

$$\text{III. } 2\,[SiO_2 \cdot Al_2O_3 \cdot 2\,H_2O]_{amorphous} \rightarrow 2\,[SiO_2 + Al_2O_3]_{amorphous} + 2\,H_2O_{vapour}$$

Variations in the bond of OH groups of the silicate lattice could also be demonstrated by measurements of the dielectric constant.

Dielectric tests

Dielectric constant DK of kaolins ground for different periods generally grows monotonously with the activation time (e. g. from 5 to 17). Heating these samples e. g. at 700 °C, determining the leaving water quantity and determining again the dielectric constant of the residual material cooled to 25 °C, its DK_i value will little depend on the activation time, and will be lower than that of the unheated sample (3,50 to 4,01).

Assuming the water removed by heating to be mixed with the heated material — provided no electric or chemical interaction between the water and the heated kaolin arises — calculated dielectric constant of the mixture would be:

$$DK_{theor} = v_v DK_v + v_i DK_i$$

where v_v and v_i are percentages by volume of water and solids in the mixture, and DK_v the dielectric constant of pure water.

In real silicate structures, however, water leaving upon heating is not present as an indifferent component but it is bound the silicate lattice in form of OH groups or possibly as strongly bound H_2O, hence, there is an important interaction between "water" and silicate structure. Accordingly, the dielectric constant DK of silicates is not additively composed of the dielectric constants of "structural" water and „anhydrous" kaolin, but it is lower than this theoretical value DK_{theor}. The lower it is, the stronger is the electrical and chemical interaction between the silicate lattice and OH groups or H_2O molecules in the crystal structure.

This interaction is expressed in terms of the "degree of depolarization" (ΔD_K°)

$$\Delta D_K^\circ = \frac{DK_{theor} - DK}{DK_{theor}}$$

(The lower is ΔD_K°, the stronger OH and H_2O are bound in the silicate structure.)

ΔD_K° values of fireclay from Szegilcng and kaolin from Seddlec (Zettlitz) have been plotted *vs.* activation time in *Fig. 13*. Degrees of depolarizatiсn of residual OH and H_2O groups monotonously decrease with activation time. Bond strength, or at leas, interaction of these groups with the silicate structure is gradually reduced or at least restricted by mechanical activation. In fireclay of originally poorer crystallinity, this process (protonization) is faster than in the well crystallized kaolin from Sedlec (Zettlitz).

Mechano-chemical test

Release of structural OH groups of kaolin, and incorporation into the xerogel structure has also been demonstrated by means of the following model test:

Gypsum previously dehydrated at 200 °C ($CaSO_4$-II) was mixed with kaolin

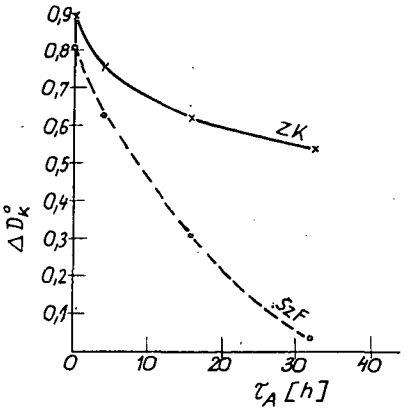

Fig. 13. Degree of depolarization of kaolin from Sedlec (Zettlitz) and fireclay from Szegi *vs.* grinding time. Curves point out the weakening of bond strength of OH and H_2O groups in the silicate structure

dried previously at 200 °C in a ratio of 65:35. Then mixture was ground for different times in a mill under vacuum.

Derivatographic curves were applied to calculate quantities of kaolin, gypsum hemihydrate and anhydrite in powders, shown in *Fig. 14* as a function of grinding time.

Part of the anhydrite seem to be transformed to hemihydrate or dehydrate durng grinding, taking the water necessary directly from the kaolin owing to the ability of a part of water to penetrate to the surrounding phase during kaolin deformation. If there is a proper counterpart (gypsum anhydrite), it will be resorbed by kaolin, however, not as structural water but as gel water bound to amorphous oxides. Thereby the amorphization of pure kaolin gets irreversible.

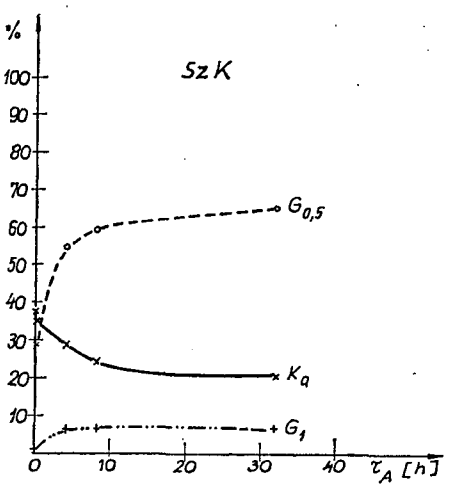

Fig. 14. Percentages of gypsum hemihydrate $G_{0,5}$ and gypsum G_1 produced by grinding of mixtures of kaolin and anhydrit, and percentage of kaolinite *Ka* calculated from the structural water content

Solubility-tests

Interesting information is furnished by the test of solubility on modification of the kaoline structure.

Tests have been made with hydrochloric acid in excess. Al, and Fe percentagesl dissolved after 2 hours of boiling have been determined and related to the total A and Fe in kaolin (l_{Al}, l_{Fe}).

Two kinds of kaolins have been tested:

One was a relatively well crystallized limonitic kaolin from Sárisáp, the other a poorly crystallized kaolin from Szegi, peculiar by its snow-whiteness in spite of its iron content over 3% in terms of Fe_2O_3.

Samples were exposed to two series of solubility tests: one series consisted in solving the unactivated samples in hydrochloric acid solutions of different dilutions, in the other series the acid dilution was kept constant (0,1 n) while kaolins were previously activated for different times. l_{Al} and l_{Fe} variations have been recorded *(Fig. 15)*. The poorly crystallized kaolin SzK seems to be *a priori* more soluble than well-crystallized *SK*, a difference prevailing for less diluted acids. At the same time, however, increase of the dissolved Al percentage seems to be concomitant with that of Fe, but the solubility of iron from the Sárisáp kaolin increases faster than that of aluminum. In this kaolin, main mass if iron is concentrated in a well soluble separate phase (limonite), irrespective of the kaolinite solubility. On the other hand, main

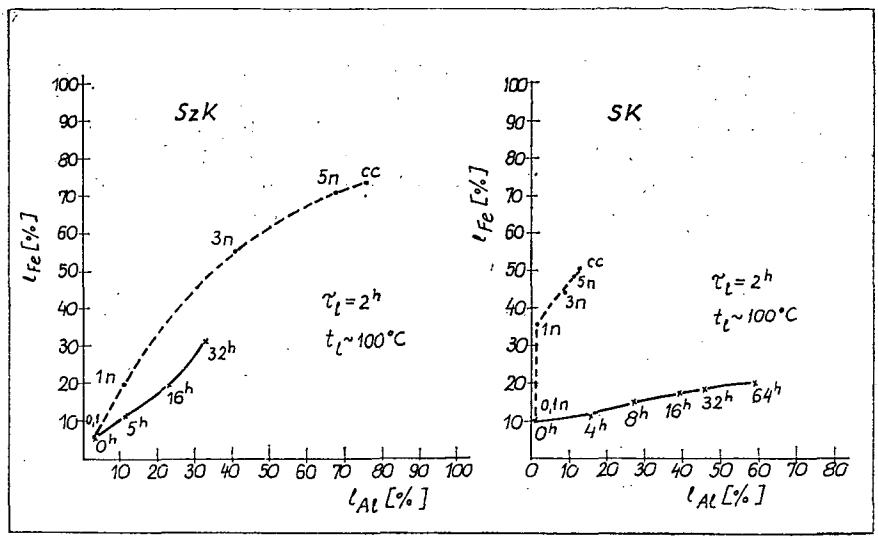

Fig. 15. Solubility of Al and Fe in kaolins from Szegi (SzK) and Sárisáp (DK) in hydrochloric acids of different *n* values after different grinding times

mass of iron in the kaolin from Szegi (about 80% of total Fe) is dissolved proportionally with Al. It can be calculated that about 20% of all the Al atoms are replaced by Fe atoms in the kaolinite lattice. Incorporation of Fe of high ion radius in place of Al of low ion radius results in a certain loosening of the kaolin lattice, in loss of the crystal structure stability.

After mechanical activation of both kaolins, solubilities of Al as well as of iron increase considerably. Solubility of iron l_{Fe}, however, is lower than that of alumi-

num I_{Al}. This difference is rather perspicuous for the Sárisáp kaolin, and may be ascribed to the inactivation (recrystallization, or at least, agglomeration into some inactivated nodes) of iron oxide in the mixture of amorphous oxides produced by mechano-chemical activation. The inactive behaviour of iron oxides forwards the selective solubility of aluminum.

MECHANO-CHEMICAL ACTIVATION

The above statements — in accordance with the publications — permit to state that supergrinding destroys crystal structure of kaolin and produces an amorphous xerogel. Transformation relies on the rupture of chemical bonds and arise of lower binding forces, material stability decreases and chemical reactivity increases. Therefore this way of activation affecting also the crystal structure is properly termed "mechano-chemical activation".

In connection with mechano-chemical activation, the following has to be pointed out:

1. Mechanical activation modifies the bonding energy, since:
   — new surfaces come about, increasing the specific surface of the system:

$$(S_1 - S_2) = \Delta S$$

   — surface forces arising on the new surface are greater, increasing the free surface activation energy of the system:

$$E_{F1} - E_{F2} = -\Delta(E_f S)$$

(E_f being the surface potential per unit area);
   — binding forces between atoms in the crystal structure, hence lattice energy of the crystal decreases:

$$E_{R1} - E_{R2} = \Delta E_R$$

Thus, overall change in the bonding energy (for 1 g of material)

$$\Delta E_K = \Delta E_R - \Delta(E_f S).$$

For the sake of simplicity — neglecting kinetic energies during grinding, heating, volume work etc. — change in the bonding energy is proportional to the change in free energy of the system:

$$k\Delta E_K = \Delta F = \Delta U - T\Delta S$$

(U=internal energy, S=entropy, k=conversion factor).

2. Three partial processes of mechano-chemical activation such as mechanical dispersion, surface activation and crystal structure changes may be independent to a degree, or at least proceed at different velocities.

This is apparent from *Fig. 16* where mechanical dispersion, surface activation and crystal structure variations have been represented as derivatives with respect to the grinding time of dispersity degree S_v, water adsorption potential ψ_v and activation energy of water release E^a_{OH}, respectively, thus, by the variation rate of characteristics of state, and plotted as a function of activation (grinding) time (τ_A).

The presented kinetic curves show the kaolins — either poorly or well-crystallized — to be ruled initially in grinding by mechanical dispersion, the speediest process.

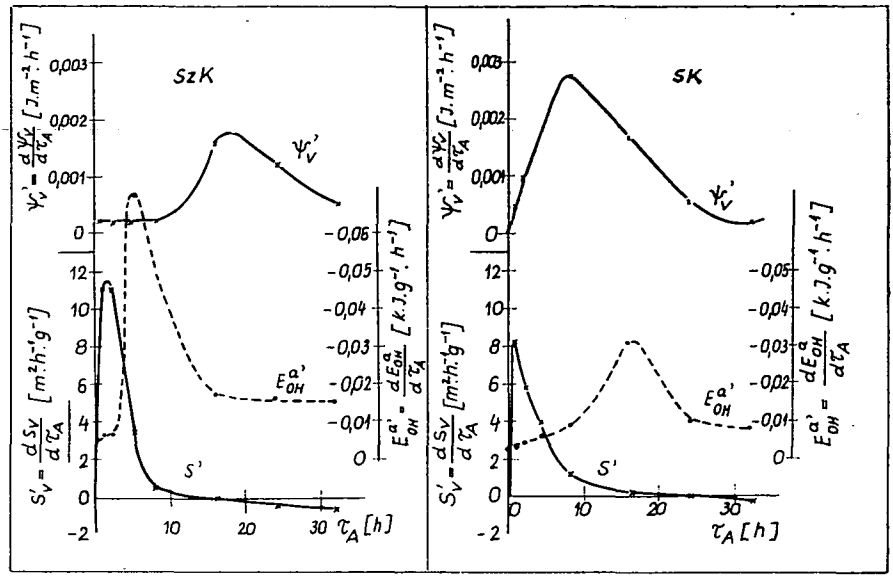

Fig. 16. Diagrams of rates of mechano-chemical activation

For sufficiently high dispersion degree, further disintegration slows down in favour of surface of crystal structure activation. The sequence is, however, variable: before surface activation the inner structure of poorly crystallized kaolin SzK gets sooner destroyed, opposite to the well-crystallized kaolin (SK).

Otherwise, various partial processes are overlapping, pointing to the statistic character of the phenomenon (activation of smaller particles preceeds that of the bigger ones, a given powder may contain any particle size).

3. Amorphization is of utmost importance in mechanical activation. *Fig. 17* shows degree of crystallinity to abruptly decrease with increasing specific surface.

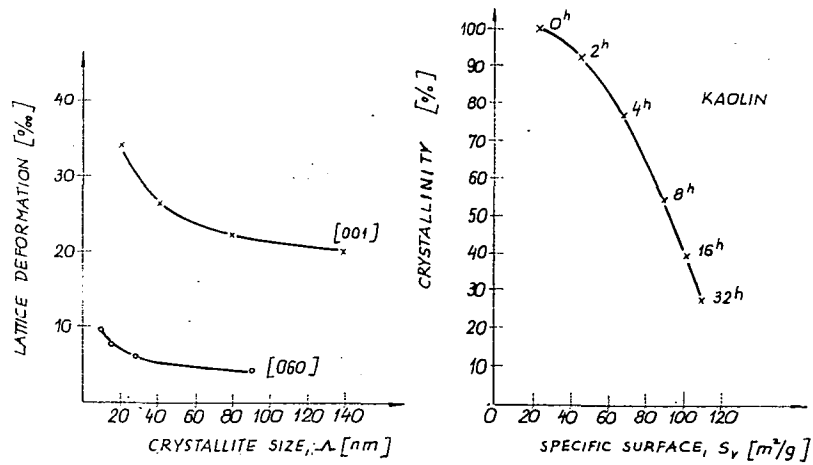

Fig. 17. Relationship between crystallite size and lattice deformation and between specific surface and degree of crystallinity.

On the other hand, with decreasing crystallite sizes, after a critical size, the lattice distortion is abruptly increasing.

This, amorphization is concomitant to the mechanical activation of adequately finelly ground crystals. Below a critical size, crystals do not break up but undergo plastic deformation. As a consequence, dislocation density grows (permanently) to a degree where X-ray reflections typical of crystalline materials are replaced by an X-ray pattern typical of "amorphous" materials.

KAOLIN-WATER SYSTEMS

After mechano-chemical activation, i. e. preliminary dry grinding, of kaolins, properties of aqueous kaolin suspensions show important changes, to be described below.

Kaolin suspensions have been tested for:

— *Particle size distribution* in 2% aqueous suspension, with a Köhn—Robinson pipette. Peptizer; 2% Na_2CO_3 solids.

— *Rheology* in a rotational viscosimeter type "Rheotest 2". Suspension concentration: 24%.

— *Methylene blue adsorption specific surface,* i. e. area accessible to relatively

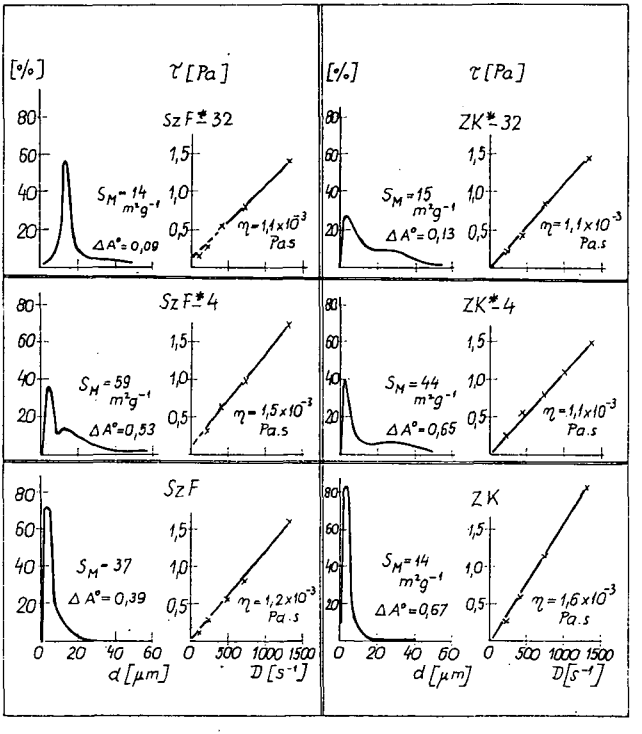

Fig. 18. Properties of aqueous solutions of fireclay from Szegi SzF and kaolin from Sedle c (Zettlitz) ZK in original conditions, and after 4 h and 32 h of activation

large-size methylene blue molecules S_M. The *degree of disaggregation* caclulated thereform is:

$$\Delta A^\circ = \frac{S_M}{S_V}$$

Changes of state in kaolin suspensions due to mechanical activation are shown in *Fig. 18*, the most important ones being:

1. Coarsening of kaolin suspensions in the activated systems due to abrupt agglomeration.

2. Coexistence of two opposite processes, i. e. mechanical dispersion and aggregation-agglomeration in the development of the methylene blue surface i. e. disaggregation degree. For instance, after 4 h of grinding, the surface S_M released in the suspension grows, but after 32 h of grinding it decreases since kaolin aggregates cannot soak, disaggregate in water. Development of the disaggregation degree, however, is a hint that the dispersity degree of the suspension is more sensitive to structural changes arising in kaolin grinding than is the "total" specific surface hence dispersity degree of the powder.

3. The above changes of the dispersity degree of aqueous systems also prevail in the evolution of rheologic properties. Mechano-chemical activation sets back the plastic properties of kaolin.

4. In addition to S_M and ΔA°, compressive strength values τ_D of kaolin-sand mixtures wet moulded then dried have been plotted in *Fig. 19*. "Dry strength" curve seems to follow mainly the curve of disaggregation degree, hence the maximum dry strength is achieved under the best disaggregation circumstances, possibly, in turn, at an optimum grinding time.

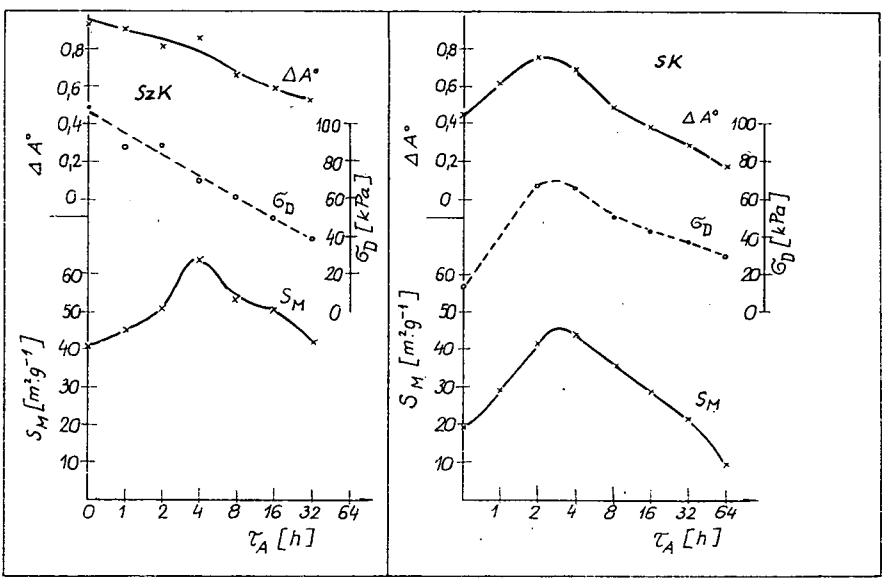

Fig. 19. "Free" specific surface S_M, degree of disaggregation ΔA° in aqueous suspensions and dry specimen strength τ_D *vs.* kaolin grinding time τ_A

EFFECT OF PREVIOUS CATION EXCHANGE ON ACTIVATION

Our tests pointed to a certain modification of processes in the mechanical activation of kaolins upon a previous ion exchange reaction of the kaolins with different cations.

Ion exchange was performed by evaporating kaolins with Li_2CO_3, Na_2CO_3 and K_2CO_3 solutions, followed by suspension in water and dialytic removal of excess electrolites.

One part of the re-exsiccated solids has been tested in original conditions. In the other part obtained after 32 h of grinding in a vibrating mill, the following characteristics were determined: vapour adsorption specific surface S_M and degree of disaggregation $\Delta A°$, percentages of "gel water" w_g and "structural water" w_{OH} as well as activation energy E_{OH} of removal of "structural water". In addition, X-ray analysis was carried out in order to determine the phase composition F of solids ground for 32 h *(Figs 20* and *21)*.

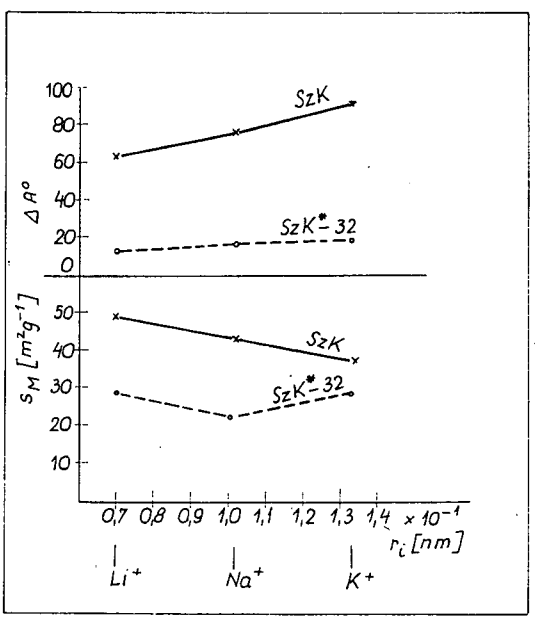

Fig. 20. "Free" specific surface S_M and degree of disaggregation $\Delta A°$ of kaolins from Szegi after ion exchange (unactivated: SzK and activated: SzK* — 32)
r_i = Radius of the exchangeable ions

The data presented show that preliminary ion exchange may modify the properties of aqueous suspensions of unactivated or activated materials. A greater importance is due, however, to the effect of quality of cations on structural changes during mechanical activation. The strongest effect is that of Li ion (causing the maximum change of E_{OH} and the least of untransformed kaolinite). This phenomenon can be attributed to the small size of Li ions permitting then to act as local depolarizers when penetrated into the silicate structure.

The most of X-ray-amorphous material was obtained from Na-kaolin while Li- and K-kaolins produced relatively more fire-clay. In conformity with the transfor-

mation sequence kaolinite — fire-clay — amorphous, Na-kaolin seems to be transformed faster, while transformation of Li- and K-kaolins seems to be stopped at the fire-clay state.

This can be explained supposing that crystal structure transformations are influenced by the disaggregation state of kaolin (considering that both disaggregation

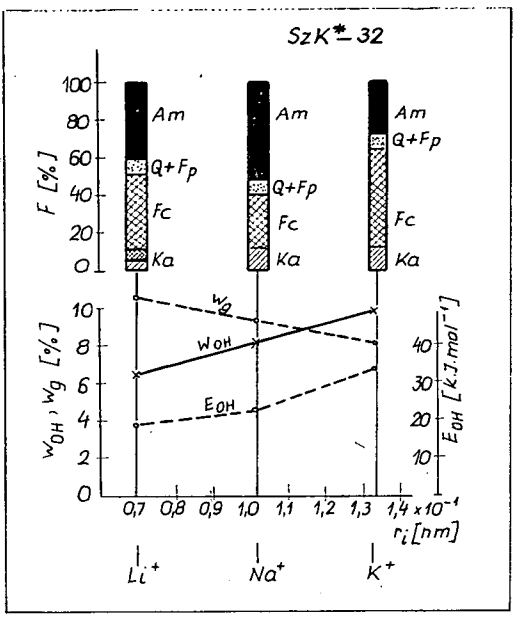

Fig. 21. Phase composition, (F%) percentages of structural water w_{OH} and gel water w_g of kaolins treated with different cations, then ground for 32 h. Activation energy E_{OH} of the release of structural water. (Am=amorphous, Q=quarz, Fc=fireclay, Ka=kaolinite)

degree and rate of crystal structure transformation of Li-kaolin are higher than those of the other two ones).

DTA curves of samples treated by different ions are shown in *Fig. 22.*

BEHAVIOUR UPON HEATING

Some examples will be quoted to illustrate the effect of mechanical activation on the behaviour of kaolins during heating:

1. Phase composition of kaolin heated to 1350 °C is not influenced by mechanical activation. Some effect was manifest after heating at 1000 °C, namely somewhat more corundum (a few %) formed from mechanically activated samples, the difference being, however, unimportant.

In case of kaolins where the structural water is weakly bound to the amorphous xerogel structure, high-temperature reactions are not controlled by mechanical activation since the gel water does not affect the composition of metakaolin structure preceeding crystalline phase developing at high temperatures. It can be noted that

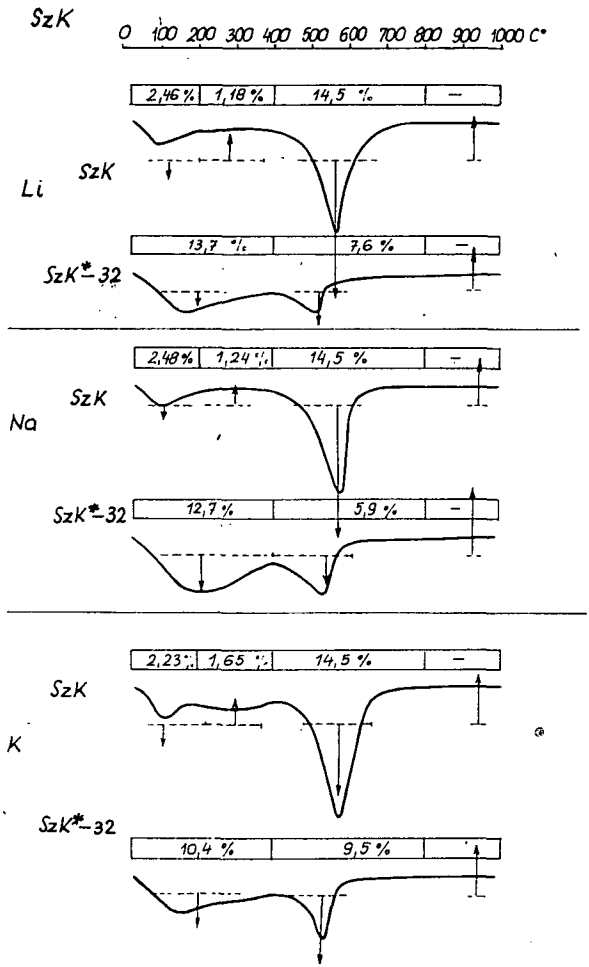

Fig. 22. DTA curves of kaolin from Szegi saturated with different cations in original condition and after grinding for 32 h; arrows indicate position and height of DTA curve maxima, number indicate mass losses

opposite phenomena were observed for other silicates such as montmorillonite, talc and pyrophillite.

2. Upon autoclave treatment (240 °C, 96 h) of kaolin mechanically activated, the valley of DTA curves between 500 to 600 °C got deeper, and the course of the curve as a whole became the same as that of a typical fireclay mineral.

3. The effect of mechanical activation on the morphology of fired kaolin is shown in *Fig. 23.*

The test procedure was the following:

Kaolin from Sedlec (Zettlitz) has been tested in original condition and after 32 h of activation. The state of the grists compacted under a pressure of 10^{-1} MPa has been plotted in the morphological diagram of state compactness — porosity — voids ratio (TPH system).

Grists were compressed under 10 MPa to specimens. Morphological changes of state may be read off the diagram.

Thereafter the specimens have been fired at 900 °C then at 1350 °C.

Final conditions at 1350 °C seem to be identical for both samples, but intermediate conditions are different. From technological aspect the most importante difference may be the lower compactness of the raw specimen as compared to that of the activated specimen made under the same pressure. This difference subsisted even after being fired at 900 °C. Thus, heating from 900 °C to 1350 °C causes a greater change in the structure of activated kaolin as compared to that of the unactivated one resulting in increased shrinkage, at technologically unfavourable property of activated kaolins.

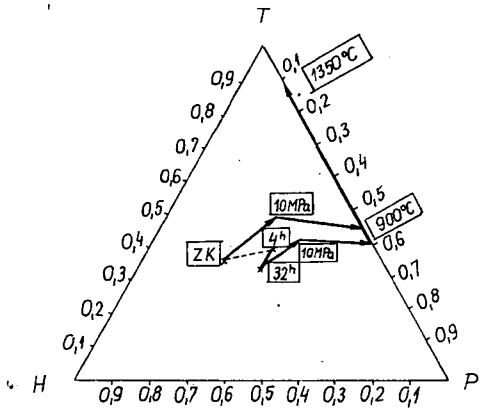

Fig. 23. Evolution of inner morphology of fired specimens pressed from kaolin powders plotted in the TPH system.

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FLOW PROPERTIES OF CHINA CLAYS IN AQUEOUS SUSPENSIONS

MÁRIA LENKEI

ABSTRACT

Aqueous suspensions of China clays of different origin were studied to observe the effect of mineralogy, crystallinity on the flow properties. Face-to-face aggregates and their face-to-edge flocs were observed by micrographs and rotational viscometry. The yield stress of suspensions is proportional to the *n*th power of the solid content, the value of *n* depends on the mineralogy. Positiv and negativ hysteresis of up-curves and down-curves are shown. Suspensions containing kaolinite and illite show positiv hysteresis, in the presence of montmorillonite negativ or so called thixotrop hysteresis are formed.

INTRODUCTION

China clay is usually prepared for fine ceramic bodies by wet method in which the material is dispersed with water and mixed with feldspar and quartz dispersion. The mixture is then filter-pressed or spray dried for removal of the excess of water. It is desirable that the solid concentration of the clay slip should be high enough to avoid segregation effect arising from the settling out of the coarse particles. This means a minimum limit of the viscosity, the maximum is given by the technological processes. The flow properties are reported here with results on the aqueous suspensions of china clays to show relationship between viscosity and concentration depending on the mineralogy.

EXPERIMENTAL PROCEDURES

Materials and their characterization

The quantitative mineralogical analysis of different industrial kaolins was made by X-ray method using a Rigaku Denki D 3F X-ray apparatus. IR-spectra were obtained using a Zeiss UR—10 spectrophotometer. The crystallinity index of the kaolinites was calculated from the IR-spectra by taking the ratio of the absorbances at 3630 and 3705 cm^{-1}. Grain size was mesaured by using an Andreasen pipette, the surface was characterized by methylene blue adsorption (Table 1).

Equipment and experimental techniques

The clay suspensions were prepared overnight using 50 g of clay in distilled water in a laboratory mill. After mixing 30 minutes the $D-\tau$ flow curves were obtained using rotational viscometer type Rheotest RV. Shearing stress τ (Pa) belonging to

TABLE 1

Mineralogical composition, grain size and crystallinity data of materials

China clays	Mineralogical composition (%)					grains under 5 micron	methylene blue surface m^2/g	IR spectra	
	kaolinite	illite	montmoril-lonite	quartz	X-ray amorphous			E_{3700}	Ratio of $\frac{E_{3630}}{E_{3700}}$
Standard	67	6	—	—	27	83	16	1,05	0,48
SPS	80	5	—	—	15	93	15	1,13	0,46
Sedlec (Zettlitz)	76	5	—	—	19	86	19	0,96	0,47
Grolleg	72	7	—	—	21	69	21	0,90	0,46
Osmose	73	4	—	—	23	67	22	0,91	0,48
OKA	63	—	—	11	26	82	20	0,88	0,54
RÖKA	72	8	—	7	11	69	20	0,79	0,55
BZ	32	2	—	28	38	68	14	0,55	0,57
Pomeisl	85	4	—	11	—	71	37	0,52	0,57
Kaolinovo	69	4	—	11	16	68	18	1,18	0,49
MEKA	56	—	—	23	21	62	18	0,72	0,52
Sárisáp	75	6	—	18	1	61	15	0,64	0,54
Caminau	66	5	—	—	29	60	17	0,74	0,59
Rátka	15	—	25	30	35	69	103	0,26	0,60
Illites	—	39	—	—	61	73	69	—	—
Füzérradvány I-1 I-6	—	20	—	10	70	54	56	—	—

the increasing and decreasing shearing rates $D(s^{-1})$ were determined. For characterizing flow properties the viscosity $\eta = \frac{\tau}{D}$ and the slope of the curves m, calculated by the following formula: $m = \log D_1 - \log D_2 / \log \tau_1 - \log \tau_2$.

RESULTS

The micrographs show that no individual particles but aggregates are present in the aqueous suspension of china clays *(Figs 1* and *2)*. Dispersion to a certain extent is taking place, but the primary structure being bilt closely together is always maintained along the faces *(Fig. 2)*. In these aqueous suspensions the edges and

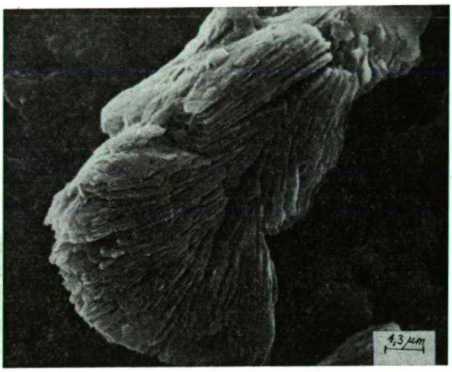

Fig. 1. Aggregate in the Sedlec (Zettlitz) kaolin-water suspension

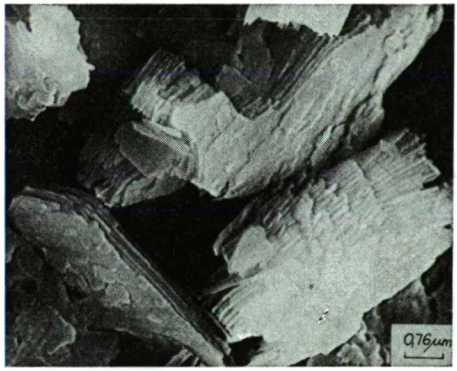

Fig. 2. Particles in the aqueous suspension of Sedlec (Zettlitz) and OKA kaolins

faces will mutually attract giving rise to a so-called "edge-to-face" flocculation. The typical flow curves of these natural flocculated clays show that different minimum stress has to be applied before these systems begin to flow *(Figs 2* and *3)*. This yield stress is proportional to the *n*th power of the solid concentration were the value of *n* is depending on the mineralogical composition of materials (Table 2, *Fig. 4*). Between the up-curves and down-curves a hysteresis loop may be observed. To avoid the misunderstanding we call positiv hysteresis in this case when the shearing stress — and viscosity — in the descending branch are the higher. In general china clay sus-

TABLE 2

Flow properties of Sedlec (Zettlitz) kaolin suspension as a function of solid concentration

Solid conc. vol. %	Yield point Pa	Viscosity mPas $D = 243\ s^{-1}$		m
		up	down	
14	10	125	130	5,38
17	21	221	226	5,74
20	50	408	433	7,58
24	75	744	744	6,17
28	140	1562	1586	5,26
31	150	3100	3200	3,50

pensions have positiv hysteresis (Table 3.). The width of the hysteresis loop obtained has been considered to be a measure of the degree of dispersity under given circumstances. These irreversible changes associated with measuring viscosity by rotational viscometer are caused by a progressive and irreversible breakdown of aggregated clay

TABLE 3

Flow properties of kaolin-water suspensions

Kaolin	Solid conc. Vol. %	Yield point Pa	Viscosity mPas $D=243\ s^{-1}$		m_I	m_{II}
			up	down		
Standard	24	150	1033	985	6,9	3,2
China clay	24	95	841	841	7,1	3,1
Sedlec (Zettlitz)	24	75	744	744	6,2	—
Grolleg	24	62	504	504	8,3	4,1
Osmose	27	80	350	560	6,2	4,2
OKA	27	100	1466	1560	4,9	1,8
RÖKA	27	70	913	937	5,1	—
BZ	27	70	1490	1514	4,9	—
Pomeisl	27	40	528	600	6,9	3,3
Kaolinovo	27	72	648	648	5,1	1,6
MEKA	27	50	860	860	4,4	1,6
Sárisáp	30	23	327	432	3,1	2,3
Caminau	34	58	793	744	3,9	2,5
Rátka	27	25	327	308	2,5	3,2
Illites						
Füzérradvány						
I-1	20	90	841	937	5,4	—
I-6	20	240	2211	2320	7,3	13,9

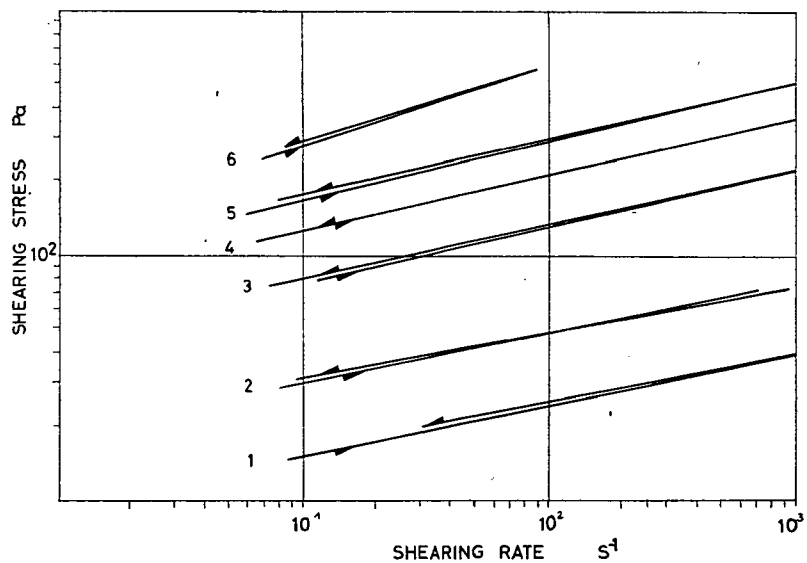

Fig. 3. Effect of dilution on the flow curves of Sedlec (Zettlitz) kaolin. Solid concentrations by vol.%: 1—14; 2—17; 3—20; 4—24; 5—28; 6—31

particles assisted by shearing. The slope of the curves is depending on the concentration (Table 2) and the composition of clays (Table 3). Two slopes of the flow curves (m_I, m_{II}) may be distinguished in general. The shear rate belonging to the inflexion is different in case of material investigated, and increases with increasing concentra-

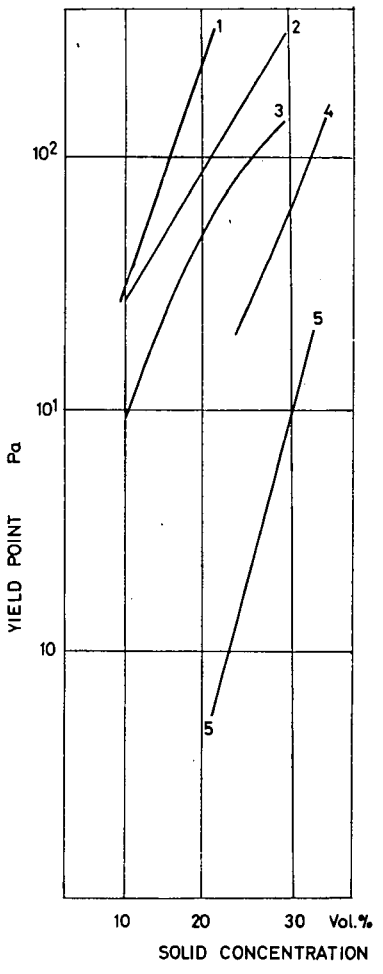

Fig. 4. The dependence of yield value from solid concentration (1- I-6, illite; 2- I-1 illite; 3- Zettlitz kaolin; 4- Meka kaolin; 5- Rátka kaolin)

tion. This reversible phenomenon shows the presence of attracting, non spherical particles in the suspensions. The yield points, viscosity and the slope values m_I show a loose comparison with crystallinity (Table 1) and the quantity of clay minerals in the clays (based on X-ray and 3700 cm^{-1} streching vibration band of the IR-spectra). The relationship between these values is disturbed by the properties of the surface.

In the presence of montmorillonite (Rátka kaolin) thixotrop hysteresis loop is formed in the aqueous suspensions. The relatively low viscosity and yield stress show peptization to a limited extent.

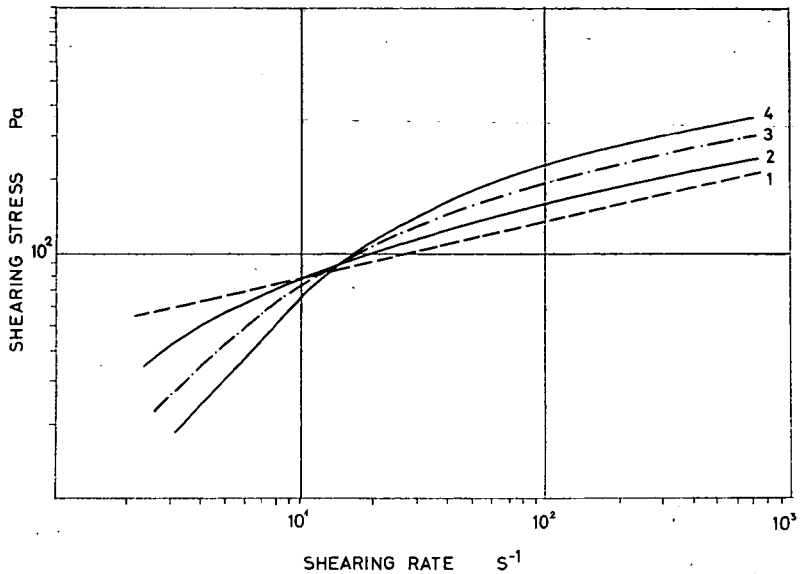

Fig. 5. Flow curve of Sedlec (Zettlitz) kaolin suspension (vol. % 20) as a function of temperature: 1—25 °C; 2—40 °C; 3—60 °C; 4—90 °C

The great part of china clays is contaminated by illite. Investigating the effect of illite on the rheological properties illite suspensions were measured. In case of the two types of the illite of Füzérradvány deposit high degree of dispersity can be observed. The hysteresis is positiv, the water content needed for a given viscosity is very high.

Under the influence of increasing temperature the flow properties of the suspen sions are changing in a characteristic manner. From the flow curve of the Sedec-(Zettlitz) kaolin *(Fig. 5)* it may be seen that at a shearing rate of 27 s^{-1} sections wilth two different slopes have been developed. Within the range of the low shearing rate the viscosity is decreasing with increasing temperatures. At higher shearing rates, however, due to the increased grade of dispersity, increasing viscosity values could be measured. Viscosity of the illite suspension — to 60 °C — was hardly changing in dependence of the increased temperature.

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COSEDIMENTATION OF KAOLINITE-MONTMORILLONITE SUSPENSIONS

F. SZÁNTÓ, Á. PATZKÓ and GY. VARJÚ

ABSTRACT

The sedimentation of kaolinite and quartz prepared from flecked kaolin was investigated in a suspension made from the montmorillonite fraction as a medium. The concentration of the suspension the pH and the quantities of certain electrolytes (NaCl and $CaCl_2$) were varied, and it was found that the character of the complex sedimentation and the structures of the sediments are influenced to a great extent by these parameters. The (aggregated) cosedimentation of montmorillonite and kaolinite could be achieved when a kaolinite suspension coagulated to some extent was added to a stable montmorillonite suspension of appropriate concentration.

The flecked kaolin from Mád-Rátka is a mixture of montmorillonite, kaolinite, quartz and feldspar. The kaolinite and the quartz appear in the form of "flecks" in the montmorillonite base material.

Since the conditions of develcpment of montmorillonite and kaolinite are very different, this is probably a reworked formation. Sedimentation of the kaolinite and quartz fractions of flecked kaolin, previously disaggregated (peptized) and fractionated, was investigated in a suspension medium prepared from the montmorillonite fraction. This served to model the geological conditions of the reworking process considered possible.

In the course of the separation of flecked kaolin, 29% pure montmorillonite, 56% kaolinite and 15% of a fraction containing chiefly quartz were obtained. In our experiments the fractions were mixed in the above ratio, and either the concentration of the suspension or the ratio of the components was changed.

As regards the conditions of formation it is well-known that kaolinite crystallizes at $pH < 7$ and montmorillonite at $pH > 7$. Consequently, in the model of the formation of flecked kaolin (presumably formed by reworking) — the pH of the kaolinite suspension was set to lower than 7. The pH of the montmorillonite suspension was about 8.2.

In parallel with this examination the influence of the ion milieu was also investigated. The experimental parameters are listed in Table 1.

The measurements were carried out at room temperature in 20 ml sedimentation tubes. Kaolinite suspensions of different concentrations and pH values to which different electrolytes and the appropriate rough quartz in calculated amount was added were layered onto montmorillonite suspensions of different concentrations. The sedimentation of suspensions made by systematic variation of the experimental parameters, and the structures of the resulting sediments, were observed through one month. It was found that in practice these systems can be divided into 3 main groups:

1. Suspensions which settle slowly and diffusely, resulting in sediments of measurable volume. This is the situation when a 1, 2 or 5% kaolinite suspension of

TABLE 1

Experimental conditions of complex sedimentation of montmorillonite and kaolinite

	Kaolinite suspension	Montmorillonite suspension
Concentration of suspension, g/100 ml	1, 2, 5	0.47, 0.95, 2.2
Suspension pH	7.5, 6, 5	8.2
NaCl-concentration, mole/dm³	0,01, 0.05, 0.1	0.05
$CaCl_2$-concentration, mole/dm³	0.01, 0.05, 0.1	

pH 7.5, containing rough quartz, is layered onto a montmorillonite suspension of relatively low concentration *(Fig. 1/a)*.

If the pH of the kaolinite suspension is set to 6, the whole suspension visibly coagulates a little, but with hardly any change in the character of the sedimentation. The kaolinite settles into the montmorillonite suspension, but coagulation initiating sedimentation with a sharp interface cannot be observed. The slight coagulation of the kaolinite suspension is not accompanied by that of the montmorillonite; this remains essentially in a peptized condition and does not settle.

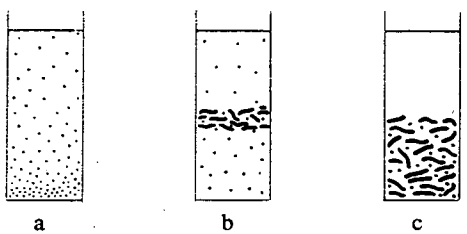

Fig. 1. a) Diffuse sedimentation, measurable volume of sediment
b) Kaolinite-quartz sediment ring on montmorillonite suspension
c) Cosedimented, coagulated montmorillonite-kaolinite-quartz suspension.

2. This group shows how large a role the concentration of the suspension may have: when the concentration of the montmorillonite suspension is 1.5% or higher, a ring-like sediment of the over-layered kaolinite suspension is formed on the surface of the montmorillonite. This ring of sediment becomes broader only when the kaolinite suspension contains quartz. The sedimentation character did not change even when the pH of the kaolinite suspension was changed or electrolytes with different concentrations, were added.

The same sedimentation character may occur with montmorillonite suspensions of lower (e. g. about 1%) concentration, if they are treated with 0.05 M calcium chloride (i. e. coagulated) before the over-layering of the kaolinite suspension *(Fig. 1/b)*.

3. This group comprises the suspensions which coagulate after being superposed on each other: they settle together at different rates, with a relatively sharp interface: their dispersion media become clear *(Fig. 1/c)*.

The kaolinite suspension coagulated in laminated layers settles relatively quickly into a montmorillonite suspension with lower than 1% concentration, and causes it to coagulate more or less: the montmorillonite, kaolinite and quartz then settle together at a lower rate. This process can also be induced by setting the kaolinite suspension to pH 5—6, but the resulting suspension settles to only a very small degree. The above phenomenon can be observed most characteristically in a system where a 2% kaolinite suspension (pH 6, containing 0.05 M calcium chloride) is layered over a 0.47% montmorillonite suspension.

It was found that cosedimentation of montmorillonite and kaolinite can be achieved when a kaolinite suspension coagulated to some extent is added to a stable montmorillonite suspension of appropriate concentration.

To summarize it can be stated that the character of the complex sedimentation of montmorillonite and kaolinite, and the structures of the sediments, are influenced by the concentration of the suspension (primarily that of montmorillonite), their pH conditions, and the quantity and nature of the electrolytes added. Some of the systems we investigated are especially noteworthy: however, further systematic and exact investigations are necessary in order to model the geological conditions more precisely.

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ADSORPTION OF LIQUID MIXTURES ON HYDROPHILIC AND ORGANOPHILIC KAOLINITE

I. DÉKÁNY

ABSTRACT

Results relating to selective sorption from methanol-benzene mixtures show that methanol is adsorbed preferentially on the original polar kaolinite and that an excess isotherm of type II is obtained. If the surface of the kaolinite is modified by alcohol treatment or is covered to various extents by HDP cations, excess isotherms of type IV results. The extent of surface modification can be characterized by the azeotropic composition of adsorption, x_1^a.

INTRODUCTION

Since kaolinite is a non-swelling clay mineral, molecules adsorbed on its surface can be bound only on the external surface, but cannot penetrate between the layers. To determine the specific surface areas of kaolinites, nitrogen and water vapour are used. Examinations of adsorption from solutions reveals that kaolinite with a polar surface primarily adsorbs polar molecules. However, if its surface is modified, the adsorption of apolar molecules may become favoured. The study of selective liquid adsorption on the surface of kaolinite means essentially determination of the adsorption excess isotherms for binary mixtures. Conclusions can be drawn from the adsorption excess isotherm with regard to the mosaic structure and surface heterogeneity of the mineral in the case of a given liquid mixture. From the value of the adsorption capacity, the specific surface of the adsorbent can be determined. In the knowledge of the adsorption capacities of liquid mixtures, it can be decided whether the disaggregation of kaolinite takes place when various liquid-pairs are applied.

The aim of the present work was to determine the adsorption properties of hydrophilic kaolinite in various liquid mixtures and, in addition, to study the mosaic structure and the surface heterogeneity of kaolinite with a modified (organophilic) surface.

MATERIALS AND METHODS

The $d \leqq 2\ \mu m$ fine fraction of kaolinite was separated from Sedlec (Zettlitz) kaolin by peptization with sodium carbonate and sedimentation. The alkaline kaolin suspension was then dialyzed to pH 6.5 to remove the excess electrolyte from the sample. The suspension was next evaporated, and the residue was dried at 378 K and sieved through a 200 mesh. The resulting kaolinite gave characteristic reflexions on X-ray diffraction examination and proved to be adequately pure for adsorption measurements.

Organophilic products were produced by ion exchange with hexadecylpyridinium chloride. On the action of the cationic tenside the suspension coagulated rapidly.

The hexadecylpyridinium kaolinite (HDP kaolinite) was dried and, in order to separate the excess tenside, extracted with methanol for 50 hours. By this procedure HDP kaolinite was produced with three different organophilicities, i. e. 2.4, 3.6 and 4.8 *mequ*/100 g.

The adsorption of liquid mixtures was examined in benzene — n-heptane and methanol — benzene at 298±0.5 K. The concentration change resulted by selective liquid sorption was determined with a Zeiss liquid-interferometer. The specific excess adsorption of the mixtures (n_1^σ) was calculated from the following equation:

$$n_1^\sigma = \frac{N_o}{m}(x_{1,0} - x_1) = n_o \Delta x_1$$

where N_0 is the total amount of the liquid mixture (in mmole), m is the mass of the adsorbent, $x_{1,0}$ is the mole fraction of component 1 before adsorption and x_1 is the equilibrium fraction in the homogeneous liquid phase.

The specific surface areas of the adsorbents were determined on the basis of the B. E. T. equation, by nitrogen-adsorption, too.

RESULTS AND DISCUSSION

The type I excess isotherms $n_1^\sigma = f(x_1)$ determined on kaolinite and its organophilic derivatives in benzene (1)-n-heptane (2) mixtures are demonstrated in *Fig. 1*. Adsorption capacities were determined with the aid of the linear individual isotherm method from the function $n_1^\sigma/x_2 = f(x_1)$ (1). Equivalent specific surface areas obtained from the adsorption capacities agree very well with the B. E. T. surface areas (Table 1) There is no essential difference between the original kaolinite and the organophilic

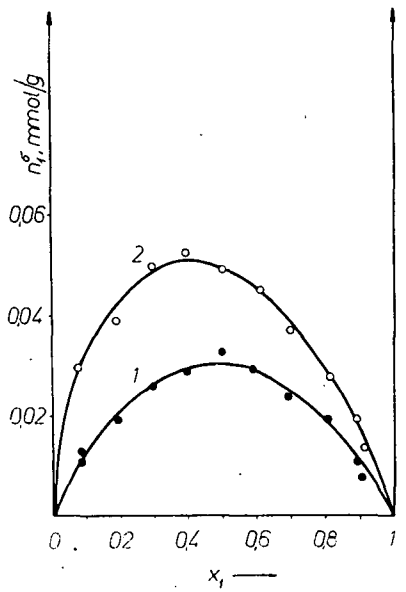

Fig. 1. Benzene(1)—n-heptane(2) excess isotherms on kaolinites. 1. original, 2. HDP-kaolinite III

TABLE 1

Results of analysis of excess isotherms

Adsorbent	HDP cation meq./100 g	$n^s_{1.0}$ mmole g^{-1}	a_s equ. $m^2\ g^{-1}$	x^a_1	Isotherm type	a_s (B. E. T.) $m^2\ g^{-1}$
liquid mixture: benzene(1) — n-heptane(2)						
kaolinite	0	0.10	18	—	I	16.2
kaolinite (treated with methanol)	0	0.12	21	—	I	21.2
HDP kaolinite III	4.8	0.16	28	—	I	24.2
liquid mixture: methanol(1) — benzene(2)						
kaolinite	0	1.05	100	—	II	16.0
kaolinite (treated with methanol)	0	1.70	162	0.59	IV	21.2
HDP kaolinite I	2.4	1.77	168	0.52	IV	—
HDP kaolinite II	3.6	1.83	174	0.46	IV	—
HDP kaolinite III	4.8	2.07	179	0.40	IV	24.2

products. On this basis the conclusion is that the adsorption of benzene from benzene — n-heptane mixtures takes place on the external surface.

The excess isotherm determined for methanol(1)-benzene(2) mixtures belongs to type II, which indicates that methanol is preferentially adsorbed on the polar surface *(Fig. 2)*. If kaolin is pre-treated with methanol in a Soxhlet-extractor for 50 hours, the course of the excess isotherm changes and an isotherm of type IV results. This change indicates that the interfacial adsorption phase the adsorption of benzene is appreciable beside that of methanol. To explain the phenomenon it must be considered that the Si-OH groups on the edges of the kaolinite layers and the Al-OH groups of the basal planes are capable of esterification during the 50-hour methanol treatment (2). Such a chemisorption effect might result in "loosening" of the compact hydrogen-bonded structure of the kaolinite and might make the layers stip on top one an other. This is indicated by the adsorption capacities, since the adsorption capacity increases compared to the dialyzed kaolinite (Table 1). The adsorption capacities of these liquid mixtures are essentially greater than in the case of a benzene — n-heptane mixture-pair. Accordingly, it can be concluded that kaolinite is capable of partial disaggregation in methanol — benzene mixtures, due to the strong adsorption of the methanol. This disaggregation is of only a slight extent, since the specific surface area derived from the excess isotherms by the SCHAY—NAGY graphical extrapolation method (3,4) is 100—160 m^2/g, i. e. 10—15% of the total basal surface area (1070 m^2/g).

The course of the excess isotherms determined on the HDP kaolinites with the three different organophilicities indicate clearly the influence of the surface modification due to the cationic tenside *(Fig. 3)*. If the surface is previously covered with HDP cations, the adsorption of the benzene becomes increasingly favoured, which means that the azeotropic composition of adsorption (x_1^a) shifts towards smaller mole fractions. Thus, methanol molecules adsorb on the free polar surface on organophilic kaolinite, while benzene is bound on a hydrophobic surface covered with HDP cations.

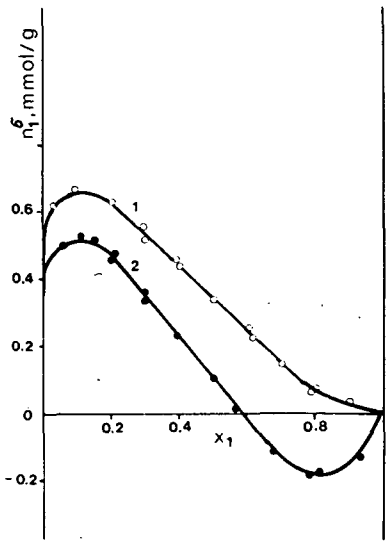

Fig. 2. Methanol(1) — benzene(2) excess isotherms on kaolinites. 1. original, 2. kaolinite treated with methanol

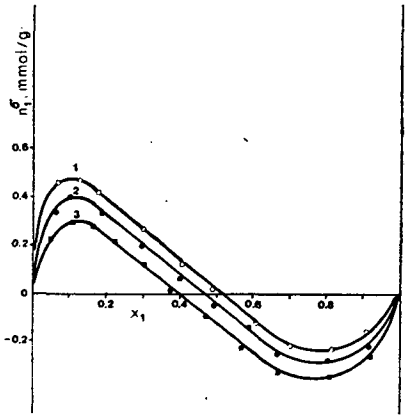

Fig. 3. Methanol(1) — benzene(2) excess isotherms on organophilic kaolinites. 1. HDP-kaolinite I, 2. HDP-kaolinite II, 3. HDP-kaolinite III

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